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# **♦EPA Methods Manual for**Compliance with the BIF Regulations

Burning Hazardous Waste in Boilers and Industrial Furnaces

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#### METHODS MANUAL

# Section 1.0 INTRODUCTION

This document presents required methods for demonstrating compliance with U.S. Environmental Protection Agency regulations for boilers and industrial furnaces (BIFs) burning hazardous waste (see 40 CFR Part 266, Subpart H). Included in this document are:

- 1. Performance Specifications for Continuous Emission Monitoring (CEM) of Carbon Monoxide, Oxygen, and Hydrocarbons in Stack Gases.
- 2. Sampling and Analytical (S&A) Methods for Multiple Metals, Hexavalent Chromium, HCl and Chlorine, Polychlorinated Dibenzop-dioxins and Dibenzofurans, and Aldehydes and Ketones.
- 3. Procedures for Estimating the Toxicity Equivalency of Chlorinated Dibenzo-p-dioxin and Dibenzofuran Congeners.
- 4. Hazardous Waste Combustion Air Quality Screening Procedures (HWCAQSP).
- 5. Simplified Land Use Classification Procedure for Compliance with Tier I and Tier II Limits.
- 6. Statistical Methodology for Bevill Residue Determinations.
- 7. Procedures for Determining Default Values for Air Pollution Control System Removal Efficiencies.
- 8. Procedures for Determining Default Values for Partitioning of Metals, Ash, and Total Chloride/Chlorine.
- 9. Alternate Methodology for Implementing Metals Controls.

Additional methods referenced in Subpart H of Part 266 but not included in this document can be found in 40 CFR Parts 60 and 61, and "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods" (SW-846).

The CEM performance specifications of Section 2.0, the S&A methods of Section 3.0 and the toxicity equivalency procedure for dioxins and furans

of Section 4.0 are required procedures for determining compliance with BIF regulations. The CEM performance specifications and the S&A methods are interim. The finalized CEM performance specifications and methods will be published in SW-846 or 40 CFR Parts 60 and 61.

#### Section 2.0

# PERFORMANCE SPECIFICATIONS FOR CONTINUOUS EMISSION MONITORING SYSTEMS

2.1 <u>Performance Specifications for Continuous Emission Monitoring of Carbon Monoxide and Oxygen for Incinerators, Boilers, and Industrial Furnaces Burning Hazardous Waste</u>

#### 2.1.1 Applicability and Principle

- 2.1.1.1 Applicability. These performance specifications apply to carbon monoxide (CO) and oxygen (O<sub>2</sub>) continuous emission monitoring systems (CEMSs) installed on incinerators, boilers, and industrial furnaces burning hazardous waste. The specifications include procedures which are intended to be used to evaluate the acceptability of the CEMS at the time of its installation or whenever specified in regulations or permits. The procedures are not designed to evaluate CEMS performance over an extended period of time. The source owner or operator is responsible for the proper calibration, maintenance, and operation of the CEMS at all times.
- 2.1.1.2 Principle. Installation and measurement location specifications, performance and equipment specifications, test and data reduction procedures, and brief quality assurance guidelines are included in the specifications. Calibration drift, relative accuracy, calibration error, and response time tests are conducted to determine conformance of the CEMS with the specifications.

#### 2.1.2 <u>Definitions</u>

2.1.2.1 Continuous Emission Monitoring System (CEMS). A continuous monitor is one in which the sample to be analyzed passes the measurement section of the analyzer without interruption, and which evaluates the detector response to the sample at least once each 15 seconds and computes and records the results at least every 60 seconds. A CEMS consists of all the equipment used to acquire data and includes the sample extraction and transport hard-

ware, the analyzer(s), and the data recording/processing hardware and soft-

- 2.1.2.2 Monitoring System Types. The specifications require CEMSs capable of accepting calibration gases. Alternative system designs may be used if approved by the Regional Administrator. There are two basic types of monitoring systems: extractive and in-situ.
- 2.1.2.2.1 Extractive. Systems that use a pump or other mechanical, pneumatic, or hydraulic means to draw a sample of the stack or flue gas and convey it to a remotely located analyzer.
- 2.1.2.2.2 In-situ. Systems that perform an analysis without removing a sample from the stack. Point in-situ analyzers place the sensing or detecting element directly in the flue gas stream. Cross-stack in-situ analyzers measure the parameter of interest by placing a source beam on one side of the stack and the detector (in single-pass instruments) or a retro-reflector (in double-pass instruments) on the other side, and measuring the parameter of interest (e.g., CO) by the attenuation of the beam by the gas in its path.
- 2.1.2.3 Instrument Measurement Range. The difference between the minimum and maximum concentration that can be measured by a specific instrument. The minimum is often stated or assumed to be zero and the range expressed only as the maximum.
- 2.1.2.4 Span or Span Value. Full scale instrument measurement range.
- 2.1.2.5 Calibration Drift (CD). The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment takes place. A CD test is performed to demonstrate the stability of the CEMS calibration over time.

- 2.1.2.6 Response Time. The time interval between the start of a step change in the system input (e.g., change of calibration gas) and the time when the data recorder displays 95 percent of the final value.
- 2.1.2.7 Accuracy. A measure of agreement between a measured value and an accepted or true value, expressed as the percentage difference between the true and measured values relative to the true value. For these performance specifications, accuracy is checked by conducting a calibration error (CE) test and a relative accuracy (RA) test. Certain facilities, such as those using solid waste or batch-fed processes, may observe long periods of almost no CO emissions with brief, high-level CO emission spikes. These facilities, as well as facilities whose CO emissions never exceed 5-10 ppm, may need to be exempted from the RA requirement because the RA test procedure cannot ensure acquisition of meaningful test results under these conditions. An alternative procedure for accuracy determination is described in Section 2.1.9.
- 2.1.2.8 Calibration Error (CE). The difference between the concentration indicated by the CEMS and the known concentration of the cylinder gas. A CE test procedure is performed to document the accuracy and linearity of the monitoring equipment over the entire measurement range.
- 2.1.2.9 Relative Accuracy (RA). A comparison of the CEMS response to a value measured by a performance test method (PTM). The RA test is used to validate the calibration technique and verify the ability of the CEMS to provide representative and accurate measurements.
- 2.1.2.10 Performance Test Method (PTM). The sampling and analysis procedure used to obtain reference measurements for comparison to CEMS measurements. The applicable test methods are Method 10, 10A, or 10B (for the determination of CO) and Method 3 or 3A (for the determination of  $O_2$ ). These methods are found in 40 CFR 60, Appendix A.
- 2.1.2.11 Performance Specification Test (PST) Period. The period during which CD, CE, response time, and RA tests are conducted.

2.1.2.12 Centroidal Area. A concentric area that is geometrically similar to the stack or duct cross section and is no greater than 1 percent of the stack or duct cross-sectional area.

#### 2.1.3 <u>Installation and Measurement Location Specifications</u>

- 2.1.3.1 CEMS Installation and Measurement Locations. shall be installed in a location in which measurements representative of the source's emissions can be obtained. The optimum location of the sample interface for the CEMS is determined by a number of factors, including ease of access for calibration and maintenance, the degree to which sample conditioning will be required, the degree to which it represents total emissions, and the degree to which it represents the combustion situation in the firebox. The location should be as free from in-leakage influences as possible and reasonably free from severe flow disturbances. The sample location should be at least two equivalent duct diameters downstream from the nearest control device, point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate occurs and at least 0.5 diameter upstream from the exhaust or control device. The equivalent duct diameter is calculated as per 40 CFR 60, Appendix A, Method 1, Section 2.1. criteria are not achievable or if the location is otherwise less than optimum, the possibility of stratification should be checked as described in Section 2.1.3.3 to determine whether the location would cause failure of the relative accuracy test.
- 2.1.3.1.1 For extractive or point in-situ CEMSs, the measurement point should be within or centrally located over the centroidal area of the tack or duct cross section.
- 2.1.3.1.2 For cross-stack CEMSs, the effective measurement path should (1) have at least 70 percent of the path within the inner 50 percent of the stack or duct cross-sectional area or (2) be centrally located over any part of the centroidal area.

- 2.1.3.1.3 Both the CO and  $\mathrm{O}_2$  monitors should be installed at the same general location. If this is not possible, they may be installed at different locations if the effluent gases at both sample locations are not stratified and there is no in-leakage of air between sampling locations.
- 2.1.3.2 Performance Test Method (PTM) Measurement Location and Traverse Points.
- 2.1.3.2.1 Select an accessible PTM measurement point at least two equivalent diameters downstream from the nearest control device, the point of CO generation, or other point at which a change in the CO concentration may occur, and at least a half equivalent diameter upstream from the effluent exhaust or control device. When pollutant concentration changes are due solely to diluent leakage (e.g., air heater leakages) and CO and  $O_2$  are simultaneously measured at the same location, one half diameter may be used in place of two equivalent diameters. The CEMS and PTM locations need not be the same.
- 2.1.3.2.2 Select traverse points that ensure acquisition of representative samples over the stack or duct cross section. At a minimum, establish a measurement line that passes through the centroidal area in the direction of any expected stratification. If this line interferes with the CEMS measurements, displace the line up to 30 cm (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area. Locate three traverse points at 17, 50, and 83 percent of the measurement line. If the measurement line is no longer than 2.4 meters and pollutant stratification is not expected, the tester may choose to locate the three traverse points on the line at 0.4, 1.2, and 2.0 meters from the stack or duct wall. This option must not be used at a site located within eight equivalent diameters downstream of a flow disturbance. The tester may select other traverse points, provided that they can be shown to the satisfaction of the Administrator to provide a representative sample over the stack or duct crosssection. Conduct all necessary PTM tests within 3 cm of the selected traverse points. Sampling must not be performed within 3 cm of the duct or stack inner wall.

2.1.3.3 Stratification Test Procedure. Stratification is defined as a difference in excess of 10 percent between the average concentration in the duct or stack and the concentration at any point more than 1.0 meter from the duct or stack wall. To determine whether effluent stratification exists, a dual probe system should be used to determine the average effluent concentration while measurements at each traverse point are being made. One probe, located at the stack or duct centroid, is used as a stationary reference point to indicate the change in effluent concentration over time. The second probe is used for sampling at the traverse points specified in Method 1, Appendix A, 40 CFR 60. The monitoring system samples sequentially at the reference and traverse points throughout the testing period for five minutes at each point.

### 2.1.4 CEMS Performance and Equipment Specifications

Table 2.1-1 summarizes the performance specifications for the CEMSs. Two sets of standards for CO are given; one for low-range and another for high-range measurements. The high-range specifications relate to measurement and quantification of short duration high concentration peaks, while the low-range specifications relate to the overall average operating condition of the burning device. The dual-range specifications can be met by using (1) one analyzer for each range, (2) a dual range unit, or (3) a single measurement range instrument capable of meeting both specifications with a single unit. Adjustments cannot be made to the analyzer between determinations of low- and high-level accuracy within the single measurement range. In the second case, when the concentration exceeds the span of the lower range, the data acquisition system recorder shall switch to the high range automatically.

2.1.4.1 CEMS Span Value. In order to measure high and low concentrations with the same or similar degree of accuracy, the maximum ranges (span values) are specified for low and high range analyzers. The span values are listed in Table 2.1-2. Tier I and Tier II format definitions are established in 40 CFR 266, Subpart H.

Table 2.1-1
PERFORMANCE SPECIFICATIONS OF CO
AND 0<sub>2</sub> MONITORS

Parameter	СО по	O <sub>2</sub> monitors	
	Low Range	High Range	
Calibration drift 24 hours	≤6 ppm¹	≤90 ppm	≤0.5% 0 <sub>2</sub>
Calibration error	≤10 ppm <sup>1</sup>	≤150 ppm	≤0.5% 0 <sub>2</sub>
Response time	≤2 min	≤2 min	≤2 min
Relative accuracy <sup>2</sup>	The greater of 10% of PTM or 10 ppm		(incorporated in CO RA calculation)

 $<sup>^1</sup> For Tier II, CD and CE are <math display="inline">\leq \!\! 3\$$  and  $\leq \!\! 5\$$  of twice the permit limit, respectively.

<sup>&</sup>lt;sup>2</sup>Expressed as the sum of the mean absolute value plus the 95% confidence interval of a series of measurements.

Table 2.1-2
CEMS SPAN VALUES FOR
CO AND 0<sub>2</sub> MONITORS

	CO monitors		O <sub>2</sub> monitors
	Low range (ppm)	High range (ppm)	
Tier I rolling average format Tier II rolling average format	200 2 x permit limit	3,000 3,000	25% 25%

- 2.1.4.2 Daily Calibration Gas Values. The owner or operator must choose calibration gas concentrations (or calibration filters for in-situ systems) that include zero and high-level calibration values for the daily calibration checks. For a single measurement range monitor, three CO calibration gas concentrations (or calibration filters for in-situ systems) shall be used, i.e., the zero and high-level concentrations of the low-range CO analyzer and the high-level concentration of the high-range CO analyzer.
- 2.1.4.2.1 The zero level for the CO or  $O_2$  analyzer may be between zero and 20 percent of the span value, e.g., 0-40 ppm for low-range CO analyzer, 0-600 ppm for the high-range CO analyzer, and 0-5 percent for the  $O_2$  analyzer (for Tier I).
- 2.1.4.2.2 The high-level concentration for the CO or  $O_2$  analyzer shall be between 50 and 90 percent of the span value, i.e., 100-180 ppm for the low-range CO analyzer, 1500-2700 ppm for the high-range CO analyzer, and 12.5-22.5 percent  $O_2$  for the  $O_2$  analyzer.
- 2.1.4.3 Data Recorder Scale. The strip chart recorder, computer, or digital recorder must be capable of recording all readings within the CEMS's measurement range and shall have a resolution of 0.5 percent of span value, i.e., 1 ppm CO for low-range CO analyzer, 15 ppm CO for high-range CO analyzer, and 0.1 percent  $O_2$  for the  $O_2$  analyzer.
- 2.1.4.4 Response Time. The response time for the CO or  $\mathrm{O}_2$  monitor shall not exceed 2 minutes to achieve 95 percent of the final stable value.
- 2.1.4.5 Calibration Drift. The CEMS must allow the determination of CD at the zero and high-level values. The CD must be determined separately for CO and  $O_2$  monitors in terms of concentration. The CO CEMS calibration response must not drift or deviate from the reference value of the calibration gas (or calibration filters for in-situ systems) by more than 3 percent of the span value after each 24-hour period of the 7-day test, i.e., 6 ppm CO for the low-range analyzer (Tier I) and 90 ppm for the high-range analyzer, at both zero and high levels. The  $O_2$  monitor calibration response must not drift or

deviate form the reference value by more than 0.5 percent  $\mathbf{0}_2$  at both zero and high levels.

- 2.1.4.6 Relative Accuracy. The result of the RA test of the CO CEMS (which incorporates the  $O_2$  monitor) must be no greater than 10 percent of the mean value of the PTM results or must be within 10 ppm CO of the PTM results, whichever is less restrictive. The ppm CO concentration shall be corrected to 7 percent  $O_2$  before calculating the RA.
- 2.1.4.7 Calibration Error. The mean difference between the CEMS and reference values at all three test points (see Table 2.1-3) must be no greater than 5 percent of span value for CO monitors (i.e., 10 ppm CO for low-range Tier I CO analyzers and 150 ppm CO for high range CO analyzers) and 0.5 percent for  $O_2$  analyzers.
- 2.1.4.8 Measurement and Recording Frequency. The sample to be analyzed shall pass through the measurement section of the analyzer without interruption. The detector shall measure the sample concentration at least once every 15 seconds. An average emission rate shall be computed and recorded at least once every 60 seconds.
- 2.1.4.9 Hourly Rolling Average Calculation. The CEMS shall calculate every minute an hourly rolling average, which is the arithmetic mean of the 60 most recent 1-minute average values.
- 2.1.4.10 Retest. If the CEMS produces results within the specified criteria, the test is successful. If the CEMS does not meet one or more of the criteria, the necessary corrections must be made and the performance tests repeated.

#### 2.1.5 Test Periods

2.1.5.1 Pretest Preparation Period. Install the CEMS, prepare the PTM test site according to the specifications in Section 2.1.3, and prepare

Table 2.1-3
CALIBRATION ERROR CONCENTRATION RANGES FOR TIER I

	GAS CONCENTRATION RANGES			
Measurement	co,			
Point	low range <sup>1</sup>	high range	O <sub>2</sub> , percent	
1	0-40	0-600	0-2	
2	60-80	900-1200	8-10	
3	140-160	2100-2400	14-16	

 $<sup>^1\</sup>mathrm{For}$  Tier II, the CE specifications for the low-range CO CEMS are 0-20%, 30-40%, and 70-80% of twice the permit limit.

the CEMS for operation and calibration according to the manufacturer's written instructions. A pretest conditioning period similar to that of the 7-day CD test is recommended to verify the operational status of the CEMS.

- 2.1.5.2 Calibration Drift Test Period. While the facility is operating under normal conditions, determine the CD at 24-hour intervals for seven consecutive days according to the procedure given in Section 2.1.6.1. All CD determinations must be made following a 24-hour period during which no unscheduled maintenance, repair, or adjustment takes place. If the combustion unit is taken out of service during the test period, record the onset and duration of the downtime and continue the calibration drift test when the unit resumes operation.
- 2.1.5.3 Relative Accuracy Test Period. Conduct the RA test according to the procedure in Section 2.1.6.4 while the facility is operating under normal conditions. RA testing for CO and  $O_2$  shall be conducted simultaneously so that the results can be calculated for CO corrected to 7 percent  $O_2$ . The RA test shall be conducted during the CD test period. It is emphasized that during the CD test period, no adjustments or repairs may be made to the CEMS other than routine calibration adjustments performed immediately following the daily CD determination.
- 2.1.5.4 Calibration Error Test and Response Time Test Periods. Conduct the CE and response time tests during the CD test period.

#### 2.1.6 Performance Specification Test Procedures

#### 2.1.6.1 Calibration Drift Test.

2.1.6.1.1 Sampling Strategy. Conduct the CD test for all monitors at 24-hour intervals for seven consecutive days using calibration gases at the two (or three, if applicable) concentration levels specified in Section 2.1.4.2. Introduce the calibration gases into the sampling system as close to the sampling probe outlet as practical. The gas shall pass through all filters, scrubbers, conditioners, and other CEMS components used during normal

- sampling. If periodic automatic or manual adjustments are made to the CEMS zero and calibration settings, conduct the CD test immediately before these adjustments, or conduct it in such a way that the CD can be determined. Record the CEMS response and subtract this value from the reference (calibration gas) value. To meet the specification, none of the differences shall exceed the limits specified in Table 2.1-1.
- 2.1.6.1.2 Calculations. Summarize the results on a data sheet. An example is shown in Figure 2.1-1. Calculate the differences between the CEMS responses and the reference values.
- 2.1.6.2 Response Time. Check the entire CEMS including sample extraction and transport, sample conditioning, gas analyses, and the data recording.
- 2.1.6.2.1 Introduce zero gas into the system. For extractive systems, introduce the calibration gases at the probe as near to the sample location as possible. For in-situ system, introduce the zero gas at a point such that all components active in the analysis are tested. When the system output has stabilized (no change greater than 1 percent of full scale for 30 seconds), switch to monitor stack effluent and wait for a stable value. Record the time (upscale response time) required to reach 95 percent of the final stable value.
- 2.1.6.2.2 Next, introduce a high-level calibration gas and repeat the above procedure. Repeat the entire procedure three times and determine the mean upscale and downscale response times. The longer of the two means is the system response time.
  - 2.1.6.3 Calibration Error Test Procedure.
- 2.1.6.3.1 Sampling Strategy. Challenge each monitor (both low- and high-range CO and  $O_2$ ) with zero gas and EPA Protocol 1 cylinder gases at three measurement points within the ranges specified in Table 2.1-3.

SOURCE:	DATE:
MONITOR:	LOCATION:
SERIAL NUMBER:	SPAN:

LOW RANGE	
HIGH RANGE	

	DAY	DATE	TIME	CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE	PERCENT OF SPAN*
	1						·
	2						
ZERO/	3						
LEVEL	4						
	5						
	6						
	7						
	1						
	2						
HIGH	3						
LEVEL	4						
	5						
	6						
	7					<u></u>	

<sup>\*</sup>Acceptance Criteria :  $\leq$  5% of span each day for seven days.

Figure 2.1-1 Calibration Drift Determination

- 2.1.6.3.1.1 If a single measurement range is used, the calibration gases used in the daily CD checks (if they are Protocol 1 cylinder gases and meet the criteria in Section 2.1.6.3.1) may be used for determining CE.
- 2.1.6.3.1.2 Operate each monitor in its normal sampling mode as nearly as possible. The calibration gas shall be injected into the sample system as close to the sampling probe outlet as practical and should pass through all CEMS components used during normal sampling. Challenge the CEMS three non-consecutive times at each measurement point and record the responses. The duration of each gas injection should be sufficient to ensure that the CEMS surfaces are conditioned.
- 2.1.6.3.2 Calculations. Summarize the results on a data sheet. An example data sheet is shown in Figure 2.1-2. Average the differences between the instrument response and the certified cylinder gas value for each gas. Calculate three CE results (five CE results for a single-range CO CEMS) according to Equation 5 (Section 2.1.7.5). No confidence coefficient is used in CE calculations.
  - 2.1.6.4 Relative Accuracy Test Procedure.
- 2.1.6.4.1 Sampling Strategy for PTM Tests. Conduct the PTM tests in such a way that they will yield measurements representative of the emissions from the source and can be correlated to the CEMS data. Although it is preferable to conduct the CO, diluent, and moisture (if needed) simultaneously, moisture measurements that are taken within a 60-minute period which includes the simultaneous CO and O<sub>2</sub> measurements may be used to calculate the dry CO concentration. (Note: At times, CEMS RA tests may be conducted during incinerator performance tests. In these cases, PTM results obtained during CEMS RA tests may be used to determine compliance with incinerator emissions limits as long as the source and test conditions are consistent with the applicable regulations.)

SOURCE:	DATE:
MONITOR:	LOCATION:
SERIAL NUMBER:	SPAN:

LOW RANGE	
HIGH RANGE	

RUN	CALIBRATION	MONITOR	DII	DIFFERENCE .		
NUMBER	VALUE	RESPONSE	Zero/Low	Mid	High	
1 - Zero						
2 - Mid						
3 - High						
4 - Mid						
5 - Zero						
6 - High						
7- Zero						
8 - Mid						
9 - High						
		MEAN DIFFERENCE =				
		CALIBRATION ERROR =	%	%	%	

Figure 2.1-2 Calibration Error Determination

#### 2.1.6.4.2 Performance Test Methods.

- 2.1.6.4.2.1 Unless otherwise specified in the regulations, Method 3 or 3A and Method 10, 10A, or 10B (40 CFR 60, Appendix A) are the test methods for  $O_2$  and CO, respectively. Make a sample traverse of at least 21 minutes, sampling for 7 minutes at each of three traverse points (see Section 3.2).
- 2.1.6.4.2.2 When the installed CEMS uses a nondispersive infrared (NDIR) analyzer, Method 10 shall use the alternative interference trap specified in Section 10.1 of the method. An option, which may be approved by the Administrator in certain cases, would allow the test to be conducted using Method 10 without the interference trap. Under this option, a laboratory interference test is performed for the analyzer prior to the field test. The laboratory interference test includes the analysis of SO<sub>2</sub>, NO, and CO<sub>2</sub> calibration gases over the range of expected effluent concentrations. Acceptable performance is indicated if the CO analyzer response to each of the gases is less than 1 percent of the applicable measurement range of the analyzer.
- 2.1.6.4.3 Number of PTM Tests. Conduct a minimum of nine sets of all necessary PTM tests. If more than nine sets are conducted, a maximum of three sets may be rejected at the tester's discretion. The total number of sets used to determine the RA must be greater than or equal to nine. All data, including the rejected data, must be reported.
- 2.1.6.4.4 Correlation of PTM and CEMS Data. The time and duration of each PTM test run and the CEMS response time should be considered in correlating the data. Use the CEMS final output (the one used for reporting) to determine an integrated average CO concentration for each PTM test run. Confirm that the pair of results are on a consistent moisture and  $O_2$  concentration basis. Each integrated CEMS value should then be compared against the corresponding average PTM value. If the CO concentration measured by the CEMS is normalized to a specified diluent concentration, the PTM results shall be normalized to the same value.

2.1.6.4.5 Calculations. Summarize the results on a data sheet. Calculate the mean of the PTM values and calculate the arithmetic differences between the PTM and the CEMS data sets. The mean of the differences, standard deviation, confidence coefficient, and CEMS RA should be calculated using Equations 1 through 4.

#### 2.1.7 Equations

2.1.7.1 Arithmetic Mean  $(\bar{\mathbf{d}})$ . Calculate  $\bar{\mathbf{d}}$  of the difference of a data set using Equation 1.

$$\bar{\mathbf{d}} = \underline{\mathbf{1}} \quad \sum_{i=1}^{n} \mathbf{d}_{i}$$
 (Eq. 1)

where:

n - Number of data points.

$$\sum_{i=1}^{n} d_{i} = \text{Algebraic sum of the individual difference } d_{i}.$$

When the mean of the differences of pairs of data is calculated, correct the data for moisture, if applicable.

2.1.7.2 Standard Deviation ( $S_d$ ). Calculate  $S_d$  using Equation 2.

$$S_{d} = \sqrt{\frac{\sum_{i=1}^{n} d_{i}^{2} - \frac{i-1}{n}}{\sum_{i=1}^{n} d_{i}}}$$
 (Eq. 2)

2.1.7.3 Confidence Coefficient (CC). Calculate the 2.5 percent error CC (one-tailed) using Equation 3.

CC = 
$$t_{0.975} \frac{S_d}{\sqrt{n}}$$
 (Eq. 3)

where:  $t_{0.975} = t$ -value (see Table 2.1-4).

Table 2.1-4 t-VALUES

nª	t <sub>0.975</sub>	n <sup>a</sup>	t <sub>0.975</sub>	nª	t <sub>0.975</sub>
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.662	15	2.145
6	2.571	11	2.228	16	2.131

 $<sup>^{\</sup>mathrm{a}}$ The values in this table are already corrected for n-l degrees of freedom. Use n equal to the number of individual values.

2.1.7.4 Relative Accuracy. Calculate the RA of a set of data using Equation 4.

$$RA = |\overline{d}| + |CC| \times 100$$

$$\overline{PTM}$$
(Eq. 4)

where:

 $|\bar{\mathbf{d}}|$  - Absolute value of the mean of the differences (Equation 1).

|CC| - Absolute value of the confidence coefficient (Equation 3).

PTM - Average reference value.

2.1.7.5 Calibration Error. Calculate CE using Equation 5.

$$CE = \left| \frac{\overline{d}}{FS} \right| \times 100$$
 (Eq. 5)

where:

d = Mean difference between CEMS response and the known reference concentration.

#### 2.1.8 Reporting

At a minimum, summarize in tabular form the results of the CD, RA, response time, and CE test, as appropriate. Include all data sheets, calculations, CEMS data records, and cylinder gas or reference material certifications.

#### 2.1.9 Alternative Procedure

- 2.1.9.1 Alternative RA Procedure Rationale. Under some operating conditions, it may not be possible to obtain meaningful results using the RA test procedure. This includes conditions where consistent, very low CO emissions or low CO emissions interrupted periodically by short duration, high level spikes are observed. It may be appropriate in these circumstances to waive the PTM RA test and substitute the following procedure.
- 2.1.9.2 Alternative RA Procedure. Conduct a complete CEMS status check following the manufacturer's written instructions. The check should

include operation of the light source, signal receiver, timing mechanism functions, data acquisition and data reduction functions, data recorders, mechanically operated functions (mirror movements, calibration gas valve operations, etc.), sample filters, sample line heaters, moisture traps, and other related functions of the CEMS, as applicable. All parts of the CEMS must be functioning properly before the RA requirement can be waived. The instruments must also have successfully passed the CE and CD requirements of the performance specifications. Substitution of the alternative procedure requires approval of the Regional Administrator.

#### 2.1.10 Quality Assurance (QA)

Proper calibration, maintenance, and operation of the CEMS is the responsibility of the owner or operator. The owner or operator must establish a QA program to evaluate and monitor CEMS performance. As a minimum, the QA program must include:

- 2.1.10.1 A daily calibration check for each monitor. The calibration must be adjusted if the check indicates the instrument's CD exceeds the specification established in Section 2.1.4.5. The gases shall be injected as close to the probe as possible to provide a check of the entire sampling system. If an alternative calibration procedure is desired (e.g., direct injections or gas cells), subject to Administrator approval, the adequacy of this alternative procedure may be demonstrated during the initial 7-day CD test. Periodic comparisons of the two procedures are suggested.
- 2.1.10.2 A daily system audit. The audit must include a review of the calibration check data, an inspection of the recording system, an inspection of the control panel warning lights, and an inspection of the sample transport and interface system (e.g., flowmeters, filters), as appropriate.
- 2.1.10.3 A quarterly calibration error (CE) test. Quarterly RA tests may be substituted for the CE test when approved by the Director on a case-by-case basis.
  - 2.1.10.4 An annual performance specification test.

#### 2.1.11 References

- 1. Jahnke, James A. and G.J. Aldina, "Handbook: Continuous Air Pollution Source Monitoring Systems," U.S. Environmental Protection Agency Technology Transfer, Cincinnati, Ohio 45268, EPA-625/6-79-005, June 1979.
- 2. "Gaseous Continuous Emissions Monitoring Systems-Performance Specification Guidelines for  $SO_2$ ,  $NO_X$ ,  $CO_2$ ,  $O_2$ , and TRS." U.S. Environmental Protection Agency OAQPS, ESED, Research Triangle Park, North Carolina, 27711, EPA-450/3-82-026, October 1982.
- 3. "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume I. Principles." U.S. Environmental Protection Agency ORD/EMSL, Research Triangle Park, North Carolina, 27711, EPA-600/9-76-006, December 1984.
- 4. Michie, Raymond, M. Jr., et. al., "Performance Test Results and Comparative Data for Designated Reference Methods for Carbon Monoxide," U.S. Environmental Protection Agency ORD/EMSL, Research Triangle Park, North Carolina, 27711, EPA-600/S4-83-013, September 1982.
- 5. Ferguson, B.B., R.E. Lester, and W.J. Mitchell, "Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery," U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 27711, EPA-600/4-82-054, August 1982.

2.2 <u>Performance Specifications for Continuous Emission Monitoring of</u>

<u>Hydrocarbons for Incinerators, Boilers, and Industrial Furnaces</u>

<u>Burning Hazardous Waste</u>

#### 2.2.1 Applicability and Principle

- 2.2.1.1 Applicability. These performance specifications apply to hydrocarbon (HC) continuous emission monitoring systems (CEMSs) installed on incinerators, boilers, and industrial furnaces burning hazardous waste. The specifications include procedures which are intended to be used to evaluate the acceptability of the CEMS at the time of its installation or whenever specified in regulations or permits. The procedures are not designed to evaluate CEMS performance over an extended period of time. The source owner or operator is responsible for the proper calibration, maintenance, and operation of the CEMS at all times.
- 2.2.1.2 Principle. A gas sample is extracted from the source through a heated sample line and heated filter (except as provided by Section 2.2.10) to a flame ionization detector (FID). Results are reported as volume concentration equivalents of propane. Installation and measurement location specifications, performance and equipment specifications, test and data reduction procedures, and brief quality assurance guidelines are included in the specifications. Calibration drift, calibration error, and response time tests are conducted to determine conformance of the CEMS with the specifications.

#### 2.2.2 <u>Definitions</u>

- 2.2.2.1 Continuous Emission Monitoring System (CEMS). The total equipment used to acquire data, which includes sample extraction and transport hardware, analyzer, data recording and processing hardware, and software. The system consists of the following major subsystems:
- 2.2.2.1.1 Sample Interface. That portion of the system that is used for one or more of the following: sample acquisition, sample transporta-

tion, sample conditioning, or protection of the analyzer from the effects of the stack effluent.

- 2.2.2.1.2 Organic Analyzer. That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.
- 2.2.2.1.3 Data Recorder. That portion of the system that records a permanent record of the measurement values. The data recorder may include automatic data reduction capabilities.
- 2.2.2.2 Instrument Measurement Range. The difference between the minimum and maximum concentration that can be measured by a specific instrument. The minimum is often stated or assumed to be zero and the range expressed only as the maximum.
- 2.2.2.3 Span or Span Value. Full scale instrument measurement range.
- 2.2.2.4 Calibration Gas. A known concentration of a gas in an appropriate diluent gas.
- 2.2.2.5 Calibration Drift (CD). The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment takes place. A CD test is performed to demonstrate the stability of the CEMS calibration over time.
- 2.2.2.6 Response Time. The time interval between the start of a step change in the system input (e.g., change of calibration gas) and the time when the data recorder displays 95 percent of the final value.
- 2.2.2.7 Accuracy. A measurement of agreement between a measured value and an accepted or true value, expressed as the percentage difference between the true and measured values relative to the true value. For these

performance specifications, accuracy is checked by conducting a calibration error (CE) test.

- 2.2.2.8 Calibration Error (CE). The difference between the concentration indicated by the CEMS and the known concentration of the cylinder gas. A CE test procedure is performed to document the accuracy and linearity of the monitoring equipment over the entire measurement range.
- 2.2.2.9 Performance Specification Test (PST) Period. The period during which CD, CE, and response time tests are conducted.
- 2.2.2.10 Centroidal Area. A concentric area that is geometrically similar to the stack or duct cross section and is no greater than 1 percent of the stack or duct cross-sectional area.

#### 2.2.3 <u>Installation and Measurement Location Specifications</u>

2.2.3.1 CEMS Installation and Measurement Locations. shall be installed in a location in which measurements representative of the source's emissions can be obtained. The optimum location of the sample interface for the CEMS is determined by a number of factors, including ease of access for calibration and maintenance, the degree to which sample conditioning will be required, the degree to which it represents total emissions, and the degree to which it represents the combustion situation in the firebox. The location should be as free from in-leakage influences as possible and reasonably free from severe flow disturbances. The sample location should be at least two equivalent duct diameters downstream from the nearest control device, point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate occurs and at least 0.5 diameter upstream from the exhaust or control device. The equivalent duct diameter is calculated as per 40 CFR 60, Appendix A, Method 1, Section 2.1. If these criteria are not achievable or if the location is otherwise less than optimum, the possibility of stratification should be investigated as described in Section 2.2.3.2. The measurement point shall be within the centroidal area of the stack or duct cross section.

2.2.3.2 Stratification Test Procedure. Stratification is defined as a difference in excess of 10 percent between the average concentration in the duct or stack and the concentration at any point more than 1.0 meter from the duct or stack wall. To determine whether effluent stratification exists, a dual probe system should be used to determine the average effluent concentration while measurements at each traverse point are being made. One probe, located at the stack or duct centroid, is used as a stationary reference point to indicate the change in effluent concentration over time. The second probe is used for sampling at the traverse points specified in 40 CFR 60 Appendix A, Method 1. The monitoring system samples sequentially at the reference and traverse points throughout the testing period for five minutes at each point.

#### 2.2.4 CEMS Performance and Equipment Specifications

If this method is applied in highly explosive areas, caution and care shall be exercised in choice of equipment and installation.

- 2.2.4.1 Flame Ionization Detector (FID) Analyzer. A heated FID analyzer capable of meeting or exceeding the requirements of these specifications. Heated systems shall maintain the temperature of the sample gas between 150°C (300°F) and 175°C (350°F) throughout the system. This requires all system components such as the probe, calibration valve, filter, sample lines, pump, and the FID to be kept heated at all times such that no moisture is condensed out of the system. (Note: As specified in the regulations, unheated HC CEMs may be considered an acceptable interim alternative monitoring technique. For additional notes, see Section 2.2.10.) The essential components of the measurement system are described below:
- 2.2.4.1.1 Sample Probe. Stainless steel, or equivalent, to collect a gas sample from the centroidal area of the stack cross-section.
- 2.2.4.1.2 Sample Line. Stainless steel or Teflon tubing to transport the sample to the analyzer. (Note: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.)

- 2.2.4.1.3 Calibration Valve Assembly. A heated three-way valve assembly to direct the zero and calibration gases to the analyzer is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.
- 2.2.4.1.4 Particulate Filter. An in-stack or out-of-stack sintered stainless steel filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter must be heated.
- 2.2.4.1.5 Fuel. The fuel specified by the manufacturer (e.g., 40 percent hydrogen/60 percent helium, 40 percent hydrogen/60 percent nitrogen gas mixtures, or pure hydrogen) should be used.
- 2.2.4.1.6 Zero Gas. High purity air with less than 0.1 parts per million by volume (ppm) HC as methane or carbon equivalent or less than 0.1 percent of the span value, whichever is greater.
- 2.2.4.1.7 Calibration Gases. Appropriate concentrations of propane gas (in air or nitrogen). Preparation of the calibration gases should be done according to the procedures in EPA Protocol 1. In addition, the manufacturer of the cylinder gas should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change by more than  $\pm 2$  percent from the certified value.
  - 2.2.4.2 CEMS Span Value. 100 ppm propane.
- 2.2.4.3 Daily Calibration Gas Values. The owner or operator must choose calibration gas concentrations that include zero and high-level calibration values.
- 2.2.4.3.1 The zero level may be between 0 and 20 ppm (zero and 20 percent of the span value).
- 2.2.4.3.2 The high-level concentration shall be between 50 and 90 ppm (50 and 90 percent of the span value).

- 2.2.4.4 Data Recorder Scale. The strip chart recorder, computer, or digital recorder must be capable of recording all readings within the CEMS's measurement range and shall have a resolution of 0.5 ppm (0.5 percent of span value).
- 2.2.4.5 Response Time. The response time for the CEMS must not exceed 2 minutes to achieve 95 percent of the final stable value.
- 2.2.4.6 Calibration Drift. The CEMS must allow the determination of CD at the zero and high-level values. The CEMS calibration response must not differ by more than  $\pm 3$  ppm ( $\pm 3$  percent of the span value) after each 24-hour period of the 7-day test at both zero and high levels.
- 2.2.4.7 Calibration Error. The mean difference between the CEMS and reference values at all three test points listed below shall be no greater than 5 ppm ( $\pm$ 5 percent of the span value).
- 2.2.4.7.1 Zero Level. Zero to 20 ppm (0 to 20 percent of span value).
- 2.2.4.7.2 Mid-Level. 30 to 40 ppm (30 to 40 percent of span value).
- 2.2.4.7.3 High-Level. 70 to 80 ppm (70 to 80 percent of span value).
- 2.2.4.8 Measurement and Recording Frequency. The sample to be analyzed shall pass through the measurement section of the analyzer without interruption. The detector shall measure the sample concentration at least once every 15 seconds. An average emission rate shall be computed and recorded at least once every 60 seconds.
- 2.2.4.9 Hourly Rolling Average Calculation. The CEMS shall calculate every minute an hourly rolling average, which is the arithmetic mean of the 60 most recent 1-minute average values.

2.2.4.10 Retest. If the CEMS produces results within the specified criteria, the test is successful. If the CEMS does not meet one or more of the criteria, necessary corrections must be made and the performance tests repeated.

#### 2.2.5 Performance Specification Test (PST) Periods

- 2.2.5.1 Pretest Preparation Period. Install the CEMS, prepare the PTM test site according to the specifications in Section 2.2.3, and prepare the CEMS for operation and calibration according to the manufacturer's written instructions. A pretest conditioning period similar to that of the 7-day CD test is recommended to verify the operational status of the CEMS.
- 2.2.5.2 Calibration Drift Test Period. While the facility is operating under normal conditions, determine the magnitude of the CD at 24-hour intervals for seven consecutive days according to the procedure given in Section 2.2.6.1. All CD determinations must be made following a 24-hour period during which no unscheduled maintenance, repair, or adjustment takes place. If the combustion unit is taken out of service during the test period, record the onset and duration of the downtime and continue the CD test when the unit resumes operation.
- 2.2.5.3 Calibration Error Test and Response Time Test Periods. Conduct the CE and response time tests during the CD test period.

#### 2.2.6 <u>Performance Specification Test Procedures</u>

#### 2.2.6.1 Calibration Drift Test.

2.2.6.1.1 Sampling Strategy. Conduct the CD test at 24-hour intervals for seven consecutive days using calibration gases at the two daily concentration levels specified in Section 2.2.4.3. Introduce the two calibration gases into the sampling system as close to the sampling probe outlet as practical. The gas shall pass through all CEM components used during normal sampling. If periodic automatic or manual adjustments are made to the CEMS

zero and calibration settings, conduct the CD test immediately before these adjustments, or conduct it in such a way that the CD can be determined. Record the CEMS response and subtract this value from the reference (calibration gas) value. To meet the specification, none of the differences shall exceed 3 ppm.

- 2.2.6.1.2 Calculations. Summarize the results on a data sheet. An example is shown in Figure 2.2-1. Calculate the differences between the CEMS responses and the reference values.
- 2.2.6.2 Response Time. The entire system including sample extraction and transport, sample conditioning, gas analyses, and the data recording is checked with this procedure.
- 2.2.6.2.1 Introduce the calibration gases at the probe as near to the sample location as possible. Introduce the zero gas into the system. When the system output has stabilized (no change greater than 1 percent of full scale for 30 sec), switch to monitor stack effluent and wait for a stable value. Record the time (upscale response time) required to reach 95 percent of the final stable value.
- 2.2.6.2.2 Next, introduce a high-level calibration gas and repeat the above procedure. Repeat the entire procedure three times and determine the mean upscale and downscale response times. The longer of the two means is the system response time.
  - 2.2.6.3 Calibration Error Test Procedure.
- 2.2.6.3.1 Sampling Strategy. Challenge the CEMS with zero gas and EPA Protocol 1 cylinder gases at measurement points within the ranges specified in Section 2.2.4.7.
- 2.2.6.3.1.1 The daily calibration gases, if Protocol 1, may be used for this test.

SOURCE:	DATE:
MONITOR:	LOCATION:
SERIAL NUMBER:	SPAN:

	DAY	DATE	TIME	CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE	PERCENT OF SPAN
ZERO/ LOW LEVEL	1						
	2						
	3						
	4						
	5						
	6						
	7						
HIGH LEVEL	1						
	2						
	3						
	4						
	5						
	6						
	7	:					

<sup>\*</sup>Acceptance Criteria : ≤ 3% of span each day for seven days.

Figure 2.2-1 Calibration Drift Determination

- 2.2.6.3.1.2 Operate the CEMS as nearly as possible in its normal sampling mode. The calibration gas should be injected into the sampling system as close to the sampling probe outlet as practical and shall pass through all filters, scrubbers, conditioners, and other monitor components used during normal sampling. Challenge the CEMS three non-consecutive times at each measurement point and record the responses. The duration of each gas injection should be for a sufficient period of time to ensure that the CEMS surfaces are conditioned.
- 2.2.6.3.2 Calculations. Summarize the results on a data sheet. An example data sheet is shown in Figure 2.2-2. Average the differences between the instrument response and the certified cylinder gas value for each gas. Calculate three CE results according to Equation 1. No confidence coefficient is used in CE calculations.

#### 2.2.7 <u>Equations</u>

2.2.7.1 Calibration Error. Calculate CE using Equation 1.

$$CE - \left| \frac{\overline{d}}{FS} \right| \times 100$$
 (Eq. 1)

where:

d - Mean difference between CEMS response and the known reference concentration.

# 2.2.8 Reporting

At a minimum, summarize in tabular form the results of the CD, response time, and CE test, as appropriate. Include all data sheets, calculations, CEMS data records, and cylinder gas or reference material certifications.

SOURCE:	DATE:
MONITOR:	LOCATION:
SERIAL NUMBER:	SPAN:

RUN NUMBER	CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE		
			Zero/Low	Mid	High
1 - Zero					
2 - Mid					
3 - High					
4 - Mid					
5 - Zero					
6 - High					
7- Zero					
8 - Mid					
9 - High					
		MEAN DIFFERENCE =			
		CALIBRATION ERROR -	%	%	%

Figure 2.2-2 Calibration Error Determination

#### 2.2.9 Quality Assurance (QA)

Proper calibration, maintenance, and operation of the CEMS is the responsibility of the owner or operator. The owner or operator must establish a QA program to evaluate and monitor CEMS performance. As a minimum, the QA program must include:

- 2.2.9.1 A daily calibration check for each monitor. The calibration must be adjusted if the check indicates the instrument's CD exceeds 3 ppm. The gases shall be injected as close to the probe as possible to provide a check of the entire sampling system. If an alternative calibration procedure is desired (e.g., direct injections or gas cells), subject to Administrator approval, the adequacy of this alternative procedure may be demonstrated during the initial 7-day CD test. Periodic comparisons of the two procedures are suggested.
- 2.2.9.2 A daily system audit. The audit must include a review of the calibration check data, an inspection of the recording system, an inspection of the control panel warning lights, and an inspection of the sample transport and interface system (e.g., flowmeters, filters), as appropriate.
- 2.2.9.3 A quarterly CE test. Quarterly RA tests may be substituted for the CE test when approved by the Director on a case-by-case basis.
  - 2.2.9.4 An annual performance specification test.

#### 2.2.10 Alternative Measurement Technique

The regulations allow gas conditioning systems to be used in conjunction with unheated HC CEMs during an interim period. This gas conditioning may include cooling to not less than 40°F and the use of condensate traps to reduce the moisture content of sample gas entering the FID to less than 2 percent. The gas conditioning system, however, must not allow the sample gas to bubble through the condensate as this would remove water soluble organic compounds. All components upstream of the conditioning system should be heated as described in Section 2.2.4 to minimize operating and maintenance problems.

# 2.2.11 References

- 1. Measurement of Volatile Organic Compounds-Guideline Series. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 27711, EPA-450/2-78-041, June 1978.
- Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency ORD/EMSL, Research Triangle Park, North Carolina, 27711, June 1978.
- Gasoline Vapor Emission Laboratory Evaluation-Part 2. U.S. Environmental Protection Agency, OAQPS, Research Triangle Park, North Carolina, 27711, EMB Report No. 76-GAS-6, August 1975.

# Section 3.0 SAMPLING AND ANALYTICAL METHODS

3.1 <u>Methodology for the Determination of Metals Emissions in Exhaust</u>

<u>Gases from Hazardous Waste Incineration and Similar Combustion</u>

Processes

# 3.1.1 Applicability and Principle

- 3.1.1.1 Applicability. This method is being developed for the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) stack emissions from hazardous waste incinerators and similar combustion processes. This method may also be used for the determination of particulate emissions following the procedures and precautions described. Modifications to the sample recovery and analysis procedures described in this protocol for the purpose of determining particulate emissions may potentially impact the front-half mercury determination. Mercury emissions should be determined using EPA Method 101A given in 40 CFR Part 61.
- 3.1.1.2 Principle. The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide in each of two impingers, and acidic potassium permanganate solution in each of two impingers. Sampling train components are recovered and digested in separate front- and back-half fractions. Materials collected in the sampling train are digested with acid solutions to dissolve organics and to remove organic constituents that may create analytical interferences. Acid digestion is performed using conventional Parr<sup>R</sup> Bomb or microwave digestion techniques. The nitric acid and hydrogen peroxide impinger solution, the acidic potassium permanganate impinger solution, the HCl rinse solution, and the probe rinse and digested filter solutions are analyzed for mercury by cold vapor atomic absorption spectroscopy (CVAAS). The nitric acid

and hydrogen peroxide solution and the probe rinse and digested filter solutions of the train catches are analyzed for Cr. Cd. Ni. Mn. Be. Cu. Zn. Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, lead, selenium, and thallium, if these elements require greater analytical sensitivity than can be obtained by ICAP. Additionally, if desired, the tester may use AAS for analyses of all metals if the resulting in-stack method detection limits meet the goal of the testing program. convenience, aliquots of each digested sample Fraction 1A plus Fraction 2A can be combined proportionally with respect to the original Fraction 1 (normally diluted to 300 ml following digestion and prior to analysis) Section 3.1.5.3.3; and concentrated Fraction 2A (normally diluted to 150 ml following digestion and prior to analysis) Section 3.1.5.3.4.1 or 3.1.5.3.4.2 for a single analytical determination. The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals and/or other quality assurance measures, as necessary, including actual sample matrix effects checks.

# 3.1.2 Range, Sensitivity, Precision, and Interferences

- 3.1.2.1 Range. For the analyses described in this methodology and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter ( $\mu$ g/ml) range in the analytical finish solution can be analyzed using this technique. Samples containing greater than approximately 50  $\mu$ g/ml of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20  $\mu$ g/ml of cadmium should be diluted to that level before analysis.
- 3.1.2.2 Analytical Sensitivity. ICAP analytical detection limits for the sample solutions (based on <u>SW-846</u>, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15

ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). The actual method detection limits are sample dependent and may vary as the sample matrix may affect the limits. The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml). The detection limit for mercury by CVAAS is approximately 0.2 ng/ml). The use of GFAAS can give added sensitivity compared to the use of direct aspiration AAS for the following metals: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

Using (1) the procedures described in this method, (2) the analytical detection limits described in the previous paragraph, (3) a volume of 300 ml, Fraction 1, for the front half and 150 ml, Fraction 2A, for the back-half samples, and (4) a stack gas sample volume of  $1.25 \, \mathrm{m}^3$ , the corresponding instack method detection limits are presented in Table A-1 and calculated as shown:

$$\frac{A \times B}{C} = D$$

where: A = analytical detection limit,  $\mu$ g/ml.

B = volume of sample prior to aliquot for analysis, ml.

 $C = \text{stack sample volume, dscm } (dsm^3).$ 

D = in-stack detection limit,  $\mu g/m^3$ .

Values in Table 3.1-1 are calculated for the front and back half and/or the total train.

To ensure optimum sensitivity in obtaining the measurements, the concentrations of target metals in the solutions are suggested to be at least ten times the analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, this concentration can be as low as approximately three times the analytical detection limit. In all cases, on at

least one sample (run) in the source test and for each metal analyzed, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition, etc., shall be used to establish the quality of the data.

Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be made more sensitive than those shown in Table A-1 for a specific test by using one or more of the following options:

- A 1-hour sampling run may collect a stack gas sampling volume of about 1.25 m<sup>3</sup>. If the sampling time is increased and 5 m<sup>3</sup> are collected, the in-stack method detection limits would be one fourth of the values shown in Table A-1 (this means that with this change, the method is four times more sensitive than a 1-hour run. Larger sample volumes (longer runs) would make it even more sensitive).
- The in-stack detection limits assume that all of the sample is digested (with exception of the aliquot for mercury) and the final liquid volumes for analysis are 300 ml, Fraction 1 for the front half and 150 ml, Fraction 2A, for the back-half sample. If the front-half volume is reduced from 300 ml to 30 ml, the front-half in-stack detection limits would be one tenth of the values shown above (ten times more sensitive). If the back-half volume is reduced from 150 ml to 25 ml, the in-stack detection limits would be one sixth of the above values. Matrix effects checks are necessary on analyses of samples and typically are of greater significance for samples that have been concentrated to less than the normal original sample volume. Reduction to a volume of less than 25 ml may not allow redissolving of the residue and may increase interference by other compounds.
- When both of the above two improvements are used on one sample at the same time, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front and back halves is reduced by a factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive).

Metal	Front-half Fraction 1 Probe and Filter	Back-half Fraction 2 Impingers 1-3	Back-half Fractions "Hg, only" Impingers 4-6	Total Train
Antimony Arsenic Barium Beryllium Cadmium Chromium Copper Lead Manganese Mercury Nickel Phosphorus Selenium Silver Thallium Zinc	7.7 (0.7)* 12.7 (0.3)* 0.5 0.07 (0.05)* 1.0 (0.02)* 1.7 (0.2)* 1.4 10.1 (0.2)* 0.5 (0.2)* 0.6** 3.6 18 18 (0.5)* 1.7 9.6 (0.2)* 0.5	3.8 (0.4)* 6.4 (0.1)* 0.3 0.04 (0.03)* 0.5 (0.01)* 0.8 (0.1)* 0.7 5.0 (0.1)* 0.2 (0.1)* 3.0** 1.8 9 9 (0.3)* 0.9 4.8 (0.1)* 0.3	2.0**	11.5 (1.1)* 19.1 (0.4)* 0.8 0.11 (0.08)* 1.5 (0.03)* 2.5 (0.3)* 2.1 15.1 (0.3)* 0.7 (0.3*) 5.6** 5.4 27 27 (0.8)* 2.6 14.4 (0.3)* 0.8

<sup>()\*</sup> Detection limit when analyzed by GFAAS.

Note: Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

<sup>\*\*</sup> Detection limit when analyzed by CVAAS, estimated for Back Half and Total Train.

- Conversely, reducing stack gas sample volume and increasing sample liquid volume will increase in-stack detection limits (the method would then be less sensitive). The front-half and back-half samples (Fractions 1A plus and 2A) can be combined proportionally (see Section 3.1.1.2 of this methodology) prior to analysis. The resultant liquid volume (excluding the mercury fractions, which must be analyzed separately) is recorded. Combining the sample as described does not allow determination (whether front or back half) of where in the train the sample was captured. The in-stack method detection limit then becomes a single value for all metals except mercury, for which the contribution of the mercury fractions must be considered.
- The above discussion assumes no blank correction. Blank corrections are discussed later in this method.
- 3.1.2.3 Precision. The precisions (relative standard deviation) for each metal detected in a method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese, and silver were not detected in the tests; however, based on the analytical sensitivity of the ICAP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.
- 3.1.2.4 Interferences. Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICAP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICAP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit (in-stack detection limit). Refer to EPA Method 6010 (SW-846) or the other analytical methods used for details on potential interferences for this method. The analyst must eliminate or reduce interferences to acceptable levels. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

# 3.1.3 Apparatus

- 3.1.3.1 Sampling Train. A schematic of the sampling train is shown in Figure 3.1-1. It is similar to the 40 CFR Part 60, Appendix A Method 5 train. The sampling train consists of the following components:
- 3.1.3.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, Sections 2.1.1 and 2.1.2, except that glass nozzles are required unless an alternate probe tip prevents the possibility of contamination or interference of the sample with its materials of construction. If a probe tip other than glass is used, no correction (because of any effect on the sample by the probe tip) of the stack sample test results can be made.
- 3.1.3.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, Sections 2.1 and 2.2, respectively.
- 3.1.3.1.3 Filter Holder. Glass, same as Method 5, Section 2.1.5, except that a Teflon filter support or other non-metallic, non-contaminating support must be used to replace the glass frit.
  - 3.1.3.1.4 Filter Heating System. Same as Method 5, Section 2.1.6.
- 3.1.3.1.5 Condenser. The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The condensing system should consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first impinger is optional and is recommended as a moisture knockout trap for use during test conditions which require such a trap. The first impinger shall be appropriately-sized, if necessary, for an expected large moisture catch and generally constructed as described for the first impinger in Method 5, Paragraph 2.1.7. The second impinger (or the first  $\frac{1}{1}$  the first impinger) shall also be constructed as described for the first impinger in Method 5. The third impinger (or the second  $\frac{1}{1}$  the second  $\frac{1}{1}$  the first impinger in Method 5. The third impinger (or the second  $\frac{1}{1}$  the same as the Greenburg Smith impinger

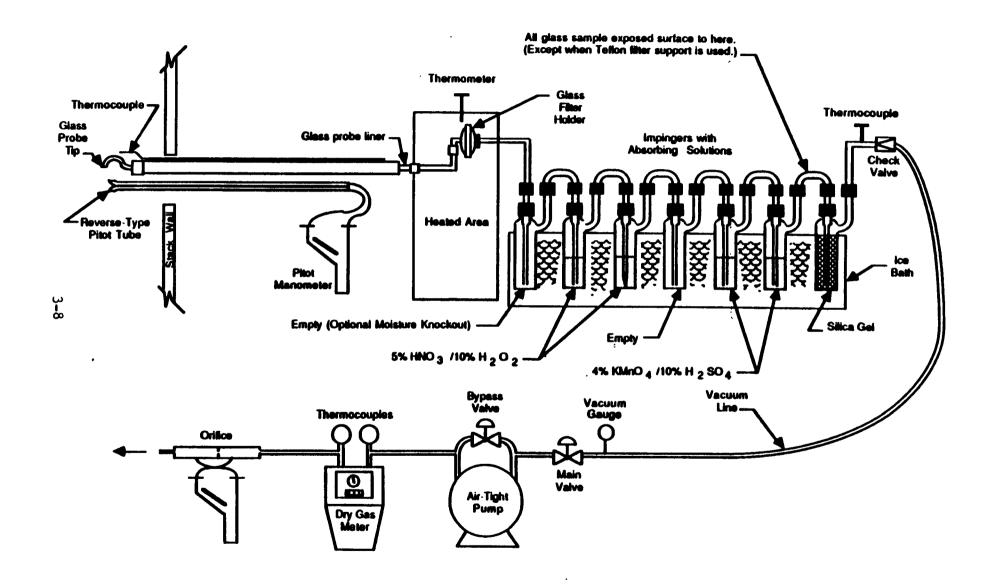


Figure 3.1-1 Schematic of multiple metals sampling train configuration.

with the standard tip described as the second impinger in Method 5, Paragraph 2.1.7. All other impingers used in the methods train are the same as the first  $\mathrm{HNO_3/H_2O_2}$  impinger described in this paragraph. In summary, the first impinger which may be optional as described in this methodology shall be empty, the second and third shall contain known quantities of a nitric acid/hydrogen peroxide solution (Section 3.1.4.2.1), the fourth shall be empty, the fifth and sixth shall contain a known quantity of acidic potassium permanganate solution (Section 3.1.4.2.2), and the last impinger shall contain a known quantity of silica gel. A thermometer capable of measuring to within  $1^{\circ}\mathrm{C}$  ( $2^{\circ}\mathrm{F}$ ) shall be placed at the outlet of the last impinger. When the moisture knockout impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not to be performed, the potassium permanganate impingers and the empty impinger preceding them are removed.

- 3.1.3.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.8 through 2.1.10, respectively.
- 3.1.3.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.
- 3.1.3.2 Sample Recovery. Same as Method 5, Sections 2.2.1 through 2.2.8 (Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:
- 3.1.3.2.1 Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs. For quantitative recovery of materials collected in the front half of the sampling train. Description of acceptable all-Teflon component brushes or swabs is to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.
- 3.1.3.2.2 Sample Storage Containers. Glass bottles with Teflonlined caps which are non-reactive to the oxidizing solutions, with a capacity

of 1000- and 500-ml, shall be used for KMnO<sub>4</sub>-containing samples and blanks. Polyethylene bottles may be used for other sample types.

- 3.1.3.2.3 Graduated Cylinder. Glass or equivalent.
- 3.1.3.2.4 Funnel. Glass or equivalent.
- 3.1.3.2.5 Labels. For identification of samples.
- 3.1.3.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.
- 3.1.3.3 Sample Preparation and Analysis. For the analysis, the following equipment is needed:
- 3.1.3.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample dilution.
  - 3.1.3.3.2 Graduated Cylinders. For preparation of reagents.
- 3.1.3.3.3 Parr<sup>R</sup> Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent).
- 3.1.3.3.4 Beakers and Watchglasses. 250-ml beakers for sample digestion with watchglasses to cover the tops.
- 3.1.3.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.
  - 3.1.3.3.6 Filter Funnels. For holding filter paper.
- 3.1.3.3.7 Whatman 541 Filter Paper (or equivalent). For filtration of digested samples.
  - 3.1.3.3.8 Disposable Pasteur Pipets and Bulbs.

- 3.1.3.3.9 Volumetric Pipets.
- 3.1.3.3.10 Analytical Balance. Accurate to within 0.1 mg.
- 3.1.3.3.11 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures.
  - 3.1.3.3.12 Hot Plates.
- 3.1.3.3.13 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.
- 3.1.3.3.13.1 Graphite Furnace Attachment. With antimony, arsenic, cadmium, lead, selenium, thallium hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). [Same as EPA SW-846 Methods 7041 (antimony), 7060 (arsenic), 7131 (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium).]
- 3.1.3.3.13.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10°C such that no condensation forms on the wall of the quartz cell. (Same as EPA Method 7470.)
- 3.1.3.3.14 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. (Same as EPA Method 6010.)

# 3.1.4 Reagents

The complexity of this methodology is such that to obtain reliable results, the testers (including analysts) should be experienced and knowledgeable in source sampling, in handling and preparing (including mixing) reagents as described, and using adequate safety procedures and protective equipment in performing this method, including sampling, mixing reagents, digestions, and

analyses. Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

- 3.1.4.1 Sampling. The reagents used in sampling are as follows:
- 3.1.4.1.1 Filters. The filters shall contain less than  $1.3~\mu g/in^2$  of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks must be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber (which meet the requirement of containing less than  $1.3~\mu g/in^2$  of each metal) filters without organic binders shall be used. The filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D2986-71 (incorporated by reference). For particulate determination in sources containing  $SO_2$  or  $SO_3$ , the filter material must be of a type that is unreactive to  $SO_2$  or  $SO_3$ , as described in EPA Method 5. Quartz fiber filters meeting these requirements are recommended for use in this method.
- 3.1.4.1.2 Water. To conform to ASTM Specification D1193.77, Type II (incorporated by reference). If necessary, analyze the water for all target metals prior to field use. All target metal concentrations should be less than 1 ng/ml.
- 3.1.4.1.3 Nitric Acid. Concentrated. Baker Instra-analyzed or equivalent.
- 3.1.4.1.4 Hydrochloric Acid. Concentrated. Baker Instra-analyzed or equivalent.
  - 3.1.4.1.5 Hydrogen Peroxide, 30 Percent (V/V).
  - 3.1.4.1.6 Potassium Permanganate.

- 3.1.4.1.7 Sulfuric Acid, Concentrated.
- 3.1.4.1.8 Silica Gel and Crushed Ice. Same as Method 5, Sections 3.1.2 and 3.1.4, respectively.
  - 3.1.4.2 Pretest Preparation for Sampling Reagents.
- 3.1.4.2.1 Nitric Acid (HNO<sub>3</sub>)/Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) Absorbing Solution, 5 Percent HNO<sub>3</sub>/10 Percent H<sub>2</sub>O<sub>2</sub>. Carefully with stirring, add 50 ml of concentrated HNO<sub>3</sub> to a 1000-ml volumetric flask containing approximately 500 ml of water, and then, carefully with stirring, add 333 ml of 30 percent H<sub>2</sub>O<sub>2</sub>. Dilute to volume (1000 ml) with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.
- 3.1.4.2.2 Acidic Potassium Permanganate (KMnO<sub>4</sub>) Absorbing Solution, 4 Percent KMnO<sub>4</sub> (W/V), 10 Percent H<sub>2</sub>SO<sub>4</sub> (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H<sub>2</sub>SO<sub>4</sub> into 800 ml of water, and add water with stirring to make a volume of 1 L: this solution is 10 percent H<sub>2</sub>SO<sub>4</sub> (V/V). Dissolve, with stirring, 40 g of KMnO<sub>4</sub> into 10 percent H<sub>2</sub>SO<sub>4</sub> (V/V) and add 10 percent H<sub>2</sub>SO<sub>4</sub> (V/V) with stirring to make a volume of 1 L: this is the acidic potassium permanganate absorbing solution. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle; these bottles shall not be fully filled and shall be vented both to relieve potential excess pressure and prevent explosion due to pressure buildup. Venting is required, but should not allow contamination of the sample; a No. 70-72 hole drilled in the container cap and Teflon liner has been used.

- 3.1.4.2.3 Nitric Acid, 0.1 N. With stirring, add 6.3 ml of concentrated  $HNO_3$  (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.
- 3.1.4.2.4 Hydrochloric Acid (HCl), 8 N. Make the desired volume of 8 N HCl in the following proportions. Carefully with stirring, add 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of Hg.
  - 3.1.4.3 Glassware Cleaning Reagents.
- 3.1.4.3.1 Nitric Acid, Concentrated. Fisher ACS grade or equivalent.
- 3.1.4.3.2 Water. To conform to ASTM Specifications D1193-77, Type II.
- 3.1.4.3.3 Nitric Acid, 10 Percent (V/V). With stirring, add 500 ml of concentrated HNO<sub>3</sub> to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.
  - 3.1.4.4 Sample Digestion and Analysis Reagents.
  - 3.1.4.4.1 Hydrochloric Acid, Concentrated.
  - 3.1.4.4.2 Hydrofluoric Acid, Concentrated.
- 3.1.4.4.3 Nitric Acid, Concentrated. Baker Instra-analyzed or equivalent.
- 3.1.4.4.4 Nitric Acid, 50 Percent (V/V). With stirring, add 125 ml of concentrated HNO<sub>3</sub> to 100 ml of water. Dilute to 250 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

- 3.1.4.4.5 Nitric Acid, 5 Percent (V/V). With stirring, add 50 ml of concentrated HNO<sub>3</sub> to 800 ml of water. Dilute to 1000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.
- 3.1.4.4.6 Water. To conform to ASTM Specifications D1193-77, Type II.
- 3.1.4.4.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See EPA Method 7470 for preparation.
  - 3.1.4.4.8 Stannous Chloride. See Method 7470.
- 3.1.4.4.9 Potassium Permanganate, 5 Percent (W/V). See Method 7470.
  - 3.1.4.4.10 Sulfuric Acid, Concentrated.
  - 3.1.4.4.11 Nitric Acid, 50 Percent (V/V).
  - 3.1.4.4.12 Potassium Persulfate, 5 Percent (W/V). See Method 7470.
  - 3.1.4.4.13 Nickel Nitrate, Ni(NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O.
  - 3.1.4.4.14 Lanthanum, Oxide,  $La_2O_3$ .
  - 3.1.4.4.15 AAS Grade Hg Standard, 1000  $\mu$ g/ml.
  - 3.1.4.4.16 AAS Grade Pb Standard, 1000  $\mu$ g/ml.
  - 3.1.4.4.17 AAS Grade As Standard, 1000  $\mu$ g/ml.
  - 3.1.4.4.18 AAS Grade Cd Standard, 1000  $\mu$ g/ml.
  - 3.1.4.4.19 AAS Grade Cr Standard, 1000  $\mu$ g/ml.

- 3.1.4.4.20 AAS Grade Sb Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.21 AAS Grade Ba Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.22 AAS Grade Be Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.23 AAS Grade  $C\mu$  Standard, 1000  $\mu g/ml$ .
- 3.1.4.4.24 AAS Grade Mn Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.25 AAS Grade Ni Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.26 AAS Grade P Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.27 AAS Grade Se Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.28 AAS Grade Ag Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.29 AAS Grade Tl Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.30 AAS Grade Zn Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.31 AAS Grade Al Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.32 AAS Grade Fe Standard, 1000  $\mu$ g/ml.
- 3.1.4.4.33 The metals standards may also be made from solid chemicals as described in EPA Method 200.7. EPA SW-846 Method 7470 or Standard Methods for the Analysis of Water and Wastewater, 15th Edition, Method 303F should be referred to for additional information on mercury standards.
- 3.1.4.4.34 Mercury Standards and Quality Control Samples. Prepare fresh weekly a 10  $\mu$ g/ml intermediate mercury standard by adding 5 ml of 1000  $\mu$ g/ml mercury stock solution to a 500-ml volumetric flask; dilute with

stirring to 500 ml by first carefully adding 20 ml of 15 percent  $HNO_3$  and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working mercury standard solution fresh daily: add 5 ml of the 10  $\mu$ g/ml intermediate standard to a 250-ml volumetric flask and dilute to 250 ml with 5 ml of 4 percent  $KMnO_4$ , 5 ml of 15 percent  $HNO_3$ , and then water. Mix well. At least six separate aliquots of the working mercury standard solution should be used to prepare the standard curve. These aliquots should contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng mercury, respectively. Quality control samples should be prepared by making a separate 10  $\mu$ g/ml standard and diluting until in the range of the calibration.

3.1.4.4.35 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as shown below.

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

<u>Solution</u>	Elements		
I	As, Be, Cd, Mn, Pb, Se, Zn		
II	Ba, Cu, Fe		
III	Al, Cr, Ni		
IV	Ag, P, Sb, Tl		

Prepare these standards by combining and diluting the appropriate volumes of the 1000  $\mu$ g/ml solutions with 5 percent nitric acid. A minimum of one standard and a blank can be used to form each calibration curve. However, a separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve should be prepared. Suggested standard levels are 25  $\mu$ g/ml for Al, Cr, and Pb, 15  $\mu$ g/ml for Fe, and 10  $\mu$ g/ml for the remaining elements. Standards containing less than 1  $\mu$ g/ml of metal should be prepared daily. Standards containing greater than 1  $\mu$ g/ml of metal should be stable for a minimum of 1 to 2 weeks.

3.1.4.4.36 Graphite Furnace AAS Standards. Antimony, arsenic, cadmium, lead, selenium, and thallium. Prepare a 10  $\mu$ g/ml standard by adding 1 ml of 1000  $\mu$ g/ml standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent nitric acid. For graphite furnace AAS, the

standards must be matrix matched. Prepare a 100 ng/ml standard by adding 1 ml of the 10  $\mu$ g/ml standard to a 100-ml volumetric flask and dilute to 100 ml with the appropriate matrix solution. Other standards should be prepared by dilution of the 100 ng/ml standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Quality control samples should be prepared by making a separate 10  $\mu$ g/ml standard and diluting until it is in the range of the samples. Standards containing less than 1  $\mu$ g/ml of metal should be prepared daily. Standards containing greater than 1  $\mu$ g/ml of metal should be stable for a minimum of 1 to 2 weeks.

#### 3.1.4.4.37 Matrix Modifiers.

- 3.1.4.4.37.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of Ni(NO<sub>3</sub>)<sub>2</sub>.  $6H_2O$  in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.
- 3.1.4.4.37.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of the 1 percent nickel nitrate solution from Section 4.4.37.1 above to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for As.
- 3.1.4.4.37.3 Lanthanum. Carefully dissolve 0.5864 g of  $\text{La}_2\text{O}_3$  in 10 ml of concentrated  $\text{HNO}_3$  and dilute the solution by adding it with stirring to approximately 50 ml of water, and then dilute to 100 ml with water. Mix well. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for Pb.

#### 3.1.5 Procedure

3.1.5.1 Sampling. The complexity of this method is such that, to obtain reliable results, testers and analysts should be trained and experienced with the test procedures, including source sampling, reagent preparation and handling, sample handling, analytical calculations, reporting, and

descriptions specifically at the beginning of and throughout Section 3.1.4 and all other sections of this methodology.

- 3.1.5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with water. All glassware should then be soaked in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled for sampling.
- 3.1.5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.
- 3.1.5.1.3 Preparation of Sampling Train. Follow the same general procedures given in Method 5, Section 4.1.3, except place 100 ml of the nitric acid/hydrogen peroxide solution (Section 3.1.4.2.1) in each of the two  $\mathrm{HNO_3/H_2O_2}$  impingers as shown in Figure 3.1-1 (normally the second and third impingers), place 100 ml of the acidic potassium permanganate absorbing solution (Section 3.1.4.2.2) in each of the two permanganate impingers as shown in Figure A-1, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

Several options are available to the tester based on the sampling requirements and conditions. The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml. If necessary, use as applicable to this methodology the procedure described in Section 7.1.1 of EPA Method 101A, 40 CFR Part 61, Appendix B, to maintain the desired color in the last permanganate impinger.

Retain for reagent blanks volumes of the nitric acid/hydrogen peroxide solution per Section 3.1.5.2.9 of this method and of the acidic potassium permanganate solution per Section 3.1.5.2.10. These reagent blanks should be labeled and analyzed as described in Section 3.1.7. Set up the sampling train as shown in Figure 3.1-1, or if mercury analysis is not to be performed in the train, then it should be modified by removing the two permanganate impingers and the impinger preceding the permanganate impingers. If necessary to ensure leak-free sampling train connections and prevent contamination Teflon tape or other non-contaminating material should be used instead of silicone grease.

<u>Precaution</u>: Extreme care should be taken to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent hydrogen peroxide from mixing with the acidic potassium permanganate.

Mercury emissions can be measured, alternatively, in a separate train which measures only mercury emissions by using EPA Method 101A with the modifications described below (and with the further modification that the permanganate containers shall be processed as described in the Precaution in Section 3.1.4.2.2 and the Note in Section 3.1.5.2.5 of this methodology). This alternative method is applicable for measurement of mercury emissions, and it may be of special interest to sources which must measure both mercury and manganese emissions.

[Section 7.2.1 of Method 101A shall be modified as follows after the 250 to  $400\text{-ml KMnO}_4$  rinse:

To remove any precipitated material and any residual brown deposits on the glassware following the permanganate rinse, rinse with approximately 100 ml of deionized distilled water, and add this water rinse carefully assuring transfer

of all loose precipitated materials from the three permanganate impingers into the permanganate Container No. 1. If no visible deposits remain after this water rinse, do not rinse with 8 N HCl. However, if deposits do remain on the glassware after this water rinse, wash the impinger surfaces with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled Container No. 1.A. containing 200 ml of water as follows. Place 200 ml of water in a sample container labeled Container No. 1.A. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing all permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse, etc. Finally, pour the 25 ml of 8 N HCl rinse carefully with stirring into Container No. 1.A. Analyze the HCl rinse separately by carefully diluting with stirring the contents of Container No. 1.A. to 500 ml with deionized distilled water. Filter (if necessary) through Whatman 40 filter paper, and then analyze for mercury according to Section 7.4, except limit the aliquot size to a maximum of 10 ml. Prepare and analyze a water diluted blank 8 N HCl sample by using the same procedure as that used by Container No. 1.A., except add 5 ml of 8 N HCl with stirring to 40 ml of water, and then dilute to 100 ml with water. Then analyze as instructed for the sample from Container No. 1.A. Because the previous separate permanganate solution rinse (Section 7.2.1) and

water rinse (as modified in these guidelines) have the capability to recover a very high percentage of the mercury from the permanganate impingers, the amount of mercury in the HCl rinse in Container No. 1.A. may be very small, possibly even insignificantly small. However, add the total of any mercury analyzed and calculated for the HCl rinse sample Container No. 1.A. to that calculated from the mercury sample from Section 7.3.2 which contains the separate permanganate rinse (and water rinse as modified herein) for calculation of the total sample mercury concentration.

- 3.1.5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).
- 3.1.5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.
- 3.1.5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.
- 3.1.5.2 Sample Recovery. Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period.

The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling. This normally causes a

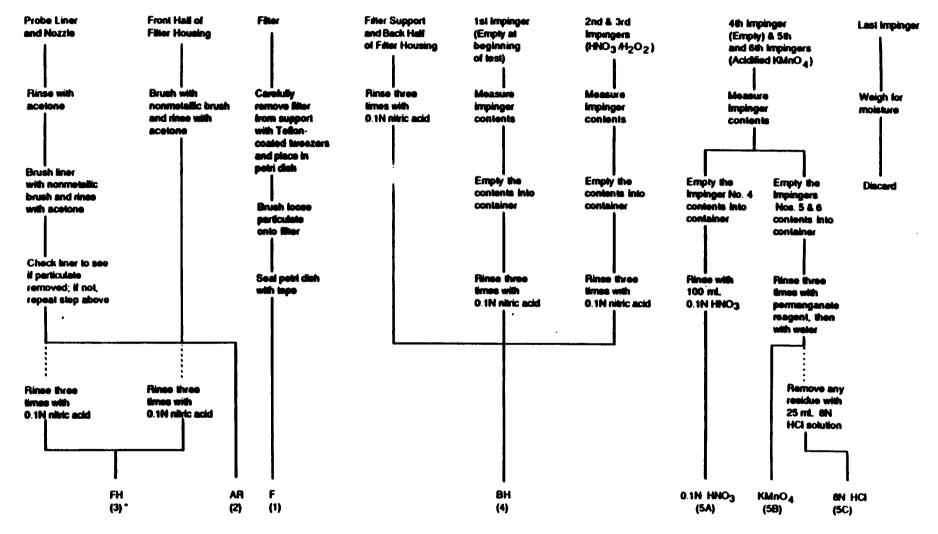
vacuum to form in the filter holder, thus causing the undesired result of drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. The sample is recovered and treated as follows (see schematic in Figure 3.1-2). Ensure that all items necessary for recovery of the sample do not contaminate it.

3.1.5.2.1 Container No. 1 (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried should be used to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.



<sup>\*</sup> Number in parentheses indicates container number

3.1.5.2.2 Container No. 2 (Acetone Rinse). NOTE: Perform Section 3.1.5.2.2 only if determination of particulate emissions are desired in addition to metals emissions. If only metals emissions are desired, skip Section 3.1.5.2.2 and go to Section 3.1.5.2.3. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting (plastic such as Teflon, polypropylene, etc. fittings are recommended to prevent contamination by metal fittings; further, if desired, a single glass piece consisting of a combined probe tip and probe liner may be used, but such a single glass piece is not a requirement of this methodology), probe liner, and front half of the filter holder by washing these components with 100 ml of acetone and placing the wash in a glass container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nonmetallic brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the sample-exposed, inside parts of the fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a nonmetallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe three times or more until none remains in the probe liner on visual inspection. Rinse the

brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Clean the inside of the front half of the filter holder by rubbing the surfaces with a nonmetallic nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container clearly to identify its contents.

- 3.1.5.2.3 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination as described in Section 3.1.5.2.2 of this method during the 0.1 N nitric acid rinse described below. Rinse the probe nozzle and fitting probe liner, and front half of the filter holder thoroughly with 100 ml of 0.1 N nitric acid and place the wash into a sample storage container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Perform the rinses as applicable and generally as described in Method 12, Section 5.2.2. Record the volume of the combined rinse. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container and clearly label the contents. Finally, rinse the nozzle, probe liner, and front half of the filter holder with water followed by acetone and discard these rinses.
- 3.1.5.2.4 Container No. 4 (Impingers 1 through 3,  $HNO_3/H_2O_2$  Impingers and Moisture Knockout Impinger, when used, Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place

the impinger solutions from impingers 1 through 3 in more than one container. Measure the liquid in the first three impingers volumetrically to within 0.5 ml using a graduated cylinder. Record the volume of liquid present. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N nitric acid using the procedure as applicable and generally as described in Method 12, Section 5.2.4. Note: The use of exactly 100 ml of 0.1 N nitric acid rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the volume. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

3.1.5.2.5 Container Nos. 5A, 5B, and 5C. 5A (0.1 N HNO<sub>3</sub>), 5B (KMnO<sub>4</sub>/ H<sub>2</sub>SO<sub>4</sub> absorbing solution), and 5C (8 N HCl rinse and dilution). (As described previously at the end of Section 3.1.3.1.5 of this method, if mercury is not being measured in this train, then impingers 4, 5, and 6, as shown in Figure A-1, are not necessary and may be eliminated.) Pour all the liquid, if any, from the impinger which was empty at the start of the run and which immediately precedes the two permanganate impingers (normally impinger No. 4) into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Sample Container No. 5A. Rinse the impinger (No. 4) with 100 ml of 0.1 N HNO<sub>3</sub> and place this into Container No. 5A.

Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this KMnO<sub>4</sub> absorbing solution stack sample from the two permanganate impingers into Container No. 5B. Using 100 ml total of fresh acidified potassium permanganate solution, rinse the two permanganate impingers and connecting glass pieces a minimum of three times and place the rinses into Container No. 5B, carefully ensuring transfer of all loose precipitated materials from the two impingers into Container No. 5B. Using 100 ml total of water, rinse the

permanganate impingers and connecting glass pieces a minimum of three times, and place the rinses into Container 5B, carefully ensuring transfer of all loose precipitated material, if any, from the two impingers into Container No. 5B. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 3.1.4.2.2 and properly prepare the bottle and clearly label the contents.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles shall not be completely filled and shall be vented to relieve potential excess pressure. Venting is required. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

If no visible deposits remain after the above described water rinse, do not rinse with 8 N HCl. However, if deposits do remain on the glassware after this water rinse, wash the impinger surfaces with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled Container No. 5C containing 200 ml of water as follows: Place 200 ml of water in a sample container labeled Container No. 5C. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing both permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully with stirring into Container No. 5C. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport.

3.1.5.2.6 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger.

The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

- 3.1.5.2.7 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a labeled container for use in the front-half field reagent blank. Seal the container.
- 3.1.5.2.8 Container No. 8A (0.1 N Nitric Acid Blank). At least once during each field test, place 300 ml of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use in the front-half and back-half field reagent blanks. Seal the container. Container No. 8B (water blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a labeled Container No. 8B. Seal the container.
- 3.1.5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Blank). At least once during each field test, place 200 ml of the 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use in the back-half field reagent blank. Seal the container.
- 3.1.5.2.10 Container No. 10 (Acidified Potassium Permanganate Blank). At least once during each field test, place 100 ml of the acidified potassium permanganate solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back-half field reagent blank for mercury analysis. Prepare the container as described in Section 3.1.5.2.5.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles shall not be

completely filled and shall be vented to relieve potential excess pressure. Venting is required. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

- 3.1.5.2.11 Container No. 11 (8 N HCl Blank). At least once during each field test, perform both of the following: Place 200 ml of water into a sample container. Pour 25 ml of 8 N HCl carefully with stirring into the 200 ml of water in the container. Mix well and seal the container.
- 3.1.5.2.12 Container No. 12 (Filter Blank). Once during each field test, place three unused blank filters from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish. These will be used in the front-half field reagent blank.
- 3.1.5.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 3.1-3.
- 3.1.5.3.1 Container No. 1 (Filter). If particulate emissions are being determined, then desiccate the filter and filter catch without added heat and weigh to a constant weight as described in Section 4.3 of Method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual microwave pressure relief vessels or Parr<sup>R</sup> Bombs. Add 6 ml of concentrated nitric acid and 4 ml of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample vessels for approximately 12-15 minutes in intervals of 1 to 2 minutes at 600 Watts. For conventional heating, heat the Parr Bombs at 140°C (285°F) for 6 hours. Cool the samples to room temperature and combine with the acid digested probe rinse as required in Section 3.1.5.3.3, below.

Container 1

Container 4

Containers 5A, 5B, & 5C

and analyses:

at 95°C for 2 h

and analyze

Figure 3.1-3 Sample preparation and analysis scheme.

Hg using CVAAS

Container 3

Container 2

Fraction 1A Fraction 1A 1 Analysis by AAS for metals found at less than 2 ug/ml. in digestate solution, if desired. Or analyze for each metal by AAS, if desired.

- Notes:
  1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Twelve to 15 minute heating times have been found to be acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by sorbent reflux within the vessel.
  - 2. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.
- 3.1.5.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated nitric acid and, carefully with stirring, quantitatively combine the resultant sample including all liquid and any particulate matter with Container No. 3 prior to beginning the following Section 3.1.5.3.3.
- 3.1.5.3.3 Container No. 3 (Probe Rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified to pH 2 by the careful addition with stirring of concentrated nitric acid. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr<sup>R</sup> Bombs by quantitatively transferring the sample to the vessel or bomb, by carefully adding the 6 ml of concentrated nitric acid and 4 ml of concentrated hydrofluoric acid

and then continuing to follow the procedures described in Section 3.1.5.3.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 3.1.5.3.1. The resultant combined sample is referred to as Fraction 1 precursor. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This dilution is Fraction 1. Measure and record the volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as Fraction 1B. Label the remaining 250-ml portion as Fraction 1A: Fraction 1A is used for ICAP or AAS analysis. Fraction 1B is used for the determination of front-half mercury.

- 3.1.5.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove a 75- to 100-ml aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as aliquot Fraction 2A. Aliquot Fraction 2A defines the volume of 2A prior to digestion. All of the aliquot Fraction 2A is digested to produce concentrated Fraction 2A. Concentrated Fraction 2A defines the volume of 2A after digestion which is normally 150 ml. concentrated Fraction 2A is analyzed for metals (except that it is not analyzed for mercury). The Fraction 2B aliquot should be prepared and analyzed for mercury as described in Section 3.1.5.4.3. Aliquot Fraction 2A shall be pH 2 or lower. If necessary, use concentrated nitric acid, by careful addition and stirring, to lower aliquot Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Next follow either the conventional or microwave digestion procedures described in Sections 3.1.5.3.4.1 and 3.1.5.3.4.2, below.
- 3.1.5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent hydrogen peroxide and heat for 20 more minutes. Add 50 ml of hot water and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate

volume for the expected metals concentrations) with water. This dilution is concentrated Fraction 2A. Measure and record the volume of the Fraction 2A solution to within 0.1 ml.

3.1.5.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent nitric acid and heat for 6 minutes in intervals of 1 to 2 minutes at 600 Watts. Allow the sample to cool. Add 10 ml of 3 percent hydrogen peroxide and heat for 2 more minutes. Add 50 ml of hot water and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution is concentrated Fraction 2A. Measure and record the volume of the Fraction 2A solution to within 0.1 ml.

Note: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

3.1.5.3.5 Container Nos. 5A, 5B, and 5C (Impingers 4, 5, and 6). Keep these samples separate from each other and measure and record the volumes of 5A and 5B separately to within 0.5 ml. Dilute sample 5C to 500 ml with water. These samples 5A, 5B, and 5C are referred to respectively as Fractions 3A, 3B, and 3C. Follow the analysis procedures described in Section 3.1.5.4.3.

Because the permanganate rinse and water rinse have the capability to recover a high percentage of the mercury from the permanganate impingers, the amount of mercury in the HCl rinse (Fraction 3C) may be very small, possibly even insignificantly small. However, as instructed in this method, add the total of any mercury measured in and calculated for the HCl rinse (Fraction 3C) to that for Fractions 1B, 2B, 3A, and 3B for calculation of the total sample mercury concentration.

- 3.1.5.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)
- 3.1.5.4 Sample Analysis. For each sampling train, seven individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 3.1-3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front half of the train. Fraction 1A is for ICAP or AAS analysis as described in Sections 3.1.5.4.1 and/or 3.1.5.4.2. Fraction 1B is for determination of front-half mercury as described in Section 3.1.5.4.3.

The back half of the train was used to prepare the third through seventh samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the moisture knockout, if used, and  $\rm HNO_3/H_2O_2$  Impingers 1 through 3. Fraction 2A is for ICAP or AAS analysis. Fraction 2B will be analyzed for mercury.

The fifth through seventh samples, labeled Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty and permanganate impingers 4, 5, and 6. These samples are analyzed for mercury as described in Section 3.1.5.4.3. The total back-half mercury catch is determined from the sum of Fraction 2B and Fractions 3A, 3B, and 3C.

3.1.5.4.1 ICAP Analysis. Fraction 1A and Fraction 2A are analyzed by ICAP using EPA <u>SW-846</u> Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. The quality control procedures described in Section 3.1.7.3.1 of this method shall be followed. Recommended wavelengths for use in the analysis are listed below:

Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Phosphorus	214.914
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

Initially, analyze all samples for the desired target metals (except mercury) plus iron and aluminum. If iron and aluminum are present in the sample, the sample may have to be diluted so that each of these elements is at a concentration of less than 50 ppm to reduce their spectral interferences on arsenic, cadmium, chromium, and lead.

<u>Note</u>: When analyzing samples in a hydrofluoric acid matrix, an alumina torch should be used; since all front-half samples will contain hydrofluoric acid, use an alumina torch.

3.1.5.4.2 AAS by Direct Aspiration and/or Graphite Furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AAS is desired, Table 3.1-2 should be used to determine

Table 3.1-2

APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE FOR AAS ANALYSIS

Metal	Technique	SW-846	Wavelength	Interferences		
<b> </b>		Method No.	(nm)	Cause	Minimization	
Sb	Aspiration	7040	217.6	1000 mg/mL Pb Ni, Cu, or acid	Use secondary wavelength of 231.1 nm; match sample & standards' acid concentra- tion or use nitrous oxide/acetylene flame	
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction	
As	Furnace	7060	193.7	Arsenic volatization	Spiked samples and add nickel nitrate solution to	
				Aluminum	digestates prior to analysis Use Zeeman background correction	
Ba	Aspiration	7080	553.6	Calcium	High hollow cathode current and narrow band set	
				Barium ionization	2 mL of KCl per 100 mL of sample	
Ве	Aspiration	7090	234.9	500 ppm Al High Mg and Si	Add 0.1% fluoride Use method of standard additions	
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects	
Cd	Aspiration	7130	228.8	Absorption and light scattering	Background correction is required	
Cd	Furnace	7131	228.8	As above Excess chloride	As above Ammonium phosphate used as a matrix modifier	
				Pipet tips	Use cadmium-free tips	
Cr	Aspiration	7190	357.9	Alkali metal	KCl ionization suppressant in samples and standards	
	•			Absorption and scatter	Consult manufacturer's literature	
Cr	Furnace	7191	357.9	200 mg/L Ca and P	All calcium nitrate for a known constant effect and to eliminate effect of phosphate	
Cu	Aspiration	7210	324.7	Absorption and scatter	Consult manufacturer's manual	

(continued)

Table 3.1-2

APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE FOR AAS ANALYSIS

Metal	Technique	SW-846	Wavelength	Interferences		
		Method No.	(nm)	Cause	Minimization	
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination	
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required	
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 uL of phosphorus acid to 1 mL of prepared sample in sampler cup	
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required	
Ní	Aspiration	7520	232.0	352.4 nm alternate Fe, Co, and Cr	Background correction required Matrix matching or nitrous-oxide/ acetylene flame	
				Nonlinear response	Sample dilution or use 352.3 nm line	
Şe	Furnace	7740	196.0	Volatility Adsorption & scatter	Spike samples and reference materials and add nickel nitrate to minimize volatilization  Background correction is required and	
!					Zeeman background correction can be useful	
Ag	Aspiration	7760	328.1	Adsorption & scatter AgCl insolube Viscosity	Background correction is required Avoid hydrochloric acid unless silver is in solution as a chloride complex Sample and standards monitored for aspiration rate	
<b>T</b> 1	Aspiration	7840	276.8		Background correction is required Hydrockless acid should not be used	
T1	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required Verify that losses are not occurring for volatization by spiked samples or standard addition; Palladium is a suitable matrix modifier	
Zn	Aspiration	7950	213.9	High Si, Cu, & P Contamination	Strontium removes Cu and phosphate Great care taken to avoid contamination	

which techniques and methods should be applied for each target metal. Table 3.1-2 should also be consulted to determine possible interferences and techniques to be followed for their minimization. Calibrate the instrument according to Section 3.1.6.3 and follow the quality control procedures specified in Section 3.1.7.3.2.

3.1.5.4.3 Cold Vapor AAS Mercury Analysis. Fraction 1B, Fraction 2B, and Fractions 3A, 3B, and 3C should be analyzed separately for mercury using cold vapor atomic absorption spectroscopy following the method outlined in EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F. Set up the calibration curve (zero to 1000 ng) as described in  $\underline{SW-846}$  Method 7470 or similar to Method 303F, using 300-ml BOD bottles instead of Erlenmeyers. Dilute separately, as described below, a 1 ml to 10 ml aliquot of each original sample to 100 ml with water. Record the amount of the aliquot used for dilution to 100 ml. If no prior knowledge exists of the expected amount of mercury in the sample, a 5-ml aliquot is suggested for the first dilution to 100 ml and analysis. To determine the stack emission value for mercury, the amount of the aliquot of the sample used for dilution and analysis is dependent on the amount of mercury in the aliquot: the total amount of mercury in the aliquot used for analysis shall be less than 1  $\mu g$ , and within the range (zero to 1000 ng) of the calibration curve. Place each sample aliquot into a separate 300-ml BOD bottle and add enough Type II water to make a total volume of 100 ml. Then analyze the 100 ml for mercury by adding to it sequentially the sample preparation solutions and performing the sample preparation and analysis as described in the procedures of SW-846 Method 7470 or Method 303F. If, during the described analysis, the reading maximum(s) are off-scale (because the aliquot of the original sample analyzed contained more mercury than the maximum of the calibration range) including the analysis of the 100-ml dilution of the 1-ml aliquot of the original sample causing a reading maximum which is off-scale, then perform the following: dilute the original sample (or a portion of it) with 0.15% HNO3 in water (1.5 ml concentrated HNO3 per liter aqueous solution) so that when a 1-ml to 10-ml aliquot of the dilution of the original sample is then further diluted to 100 ml in the BOD bottle,

and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

#### 3.1.6 Calibration

Maintain a laboratory log of all calibrations.

- 3.1.6.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).
- 3.1.6.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 3.1.4.4. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures using the above standards. The instrument calibration should be checked once per hour. If the instrument does not reproduce the concentrations of the standard within 10 percent, the complete calibration procedures should be performed.
- 3.1.6.3 Atomic Absorption Spectrometer Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses. Prepare the standards as outlined in Section 3.1.4.4. Calibrate the spectrometer using these prepared standards. Calibration procedures are also outlined in the EPA methods referred to in Table 3.1-2 and in SW-846 Method 7470 or Standard Methods for Water and Wastewater, 15th Edition, Method 303F (for mercury). Each standard curve should be run in duplicate and the mean values used to calculate the calibration line. The instrument should be recalibrated approximately once every 10 to 12 samples.

## 3.1.7 Quality Control

3.1.7.1 Sampling. Field Reagent Blanks. When analyzed, the blank samples in Container Numbers 7 through 12 produced previously in Sections

3.1.5.2.7 through 3.1.5.2.12, respectively, shall be processed, digested, and analyzed as follows: Digest and process one of the filters from Container No. 12 per Section 3.1.5.3.1, 100 ml from Container No. 7 per Section 3.1.5.3.2, and 100 ml from Container No. 8A per Section 3.1.5.3.3. This produces Fraction Blank 1A and Fraction Blank 1B from Fraction Blank 1. [If desired, the other two filters may be digested separately according to Section 3.1.5.3.1, diluted separately to 300 ml each, and analyzed separately to produce a blank value for each of the two additional filters. analyses are performed, they will produce two additional values for each of Fraction Blank 1A and Fraction Blank 1B. The three Fraction Blank 1A values will be calculated as three values of  $M_{fhb}$  in Equation 3 of Section 3.1.8.4.3, and then the three values shall be totalled and divided by 3 to become the value Mfhb to be used in the computation of Mt by Equation 3. Similarly, the three Fraction Blank 1B values will be calculated separately as three values, totalled, averaged, and used as the value for Hgfhb in Equation 8 of Section 3.1.8.5.3. The analyses of the two extra filters are optional and are not a requirement of this method, but if the analyses are performed, the results must be considered as described above. | Combine 100 ml of Container No. 8A with 200 ml of the contents of Container No. 9 and digest and process the resultant volume per Section 3.1.5.3.4. This produces concentrated Fraction Blank 2A and Fraction Blank 2B from Fraction Blank 2. A 100-ml portion of Container No. 8A is Fraction Blank 3A. Combine 100 ml of the contents of Container No. 10 with 33 ml of the contents of Container No. 8B. produces Fraction Blank 3B (use 400 ml as the volume of Fraction Blank 3B when calculating the blank value. Use the actual volumes when calculating all the other blank values). Dilute 225 ml of the contents of Container No. 11 to 500 ml with water. This produces Fraction Blank 3C. Analyze Fraction Blank 1A and Fraction Blank 2A per Section 3.1.5.4.1 and/or 3.1.5.4.2. Analyze Fraction Blank 1B, Fraction Blank 2B, and Fraction Blanks 3A, 3B, and 3C per Section 3.1.5.4.3. The analysis of Fraction Blank 1A produces the front-half reagent blank correction values for the metals except mercury; the analysis of Fraction Blank 1B produces the front-half reagent blank correction value for mercury. The analysis of concentrated Fraction Blank 2A produces the backhalf reagent blank correction values for the metals except mercury, while

separate analysis of Fraction Blanks 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for mercury.

- 3.1.7.2 An attempt may be made to determine if the laboratory reagents used in Section 3.1.5.3 caused contamination. They should be analyzed by the procedures in Section 3.1.5.4. The Administrator will determine whether the laboratory blank reagent values can be used in the calculation of the stationary source test results.
- 3.1.7.3 Quality Control Samples. The following quality control samples should be analyzed.
- 3.1.7.3.1 ICAP Analysis. Follow the quality control shown in Section 8 of Method 6010. For the purposes of a three-run test series, these requirements have been modified to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25% or analyze by the method of standard additions), one quality control sample to check the accuracy of the calibration standards (must be within 25% of calibration), and one duplicate analysis (must be within 10% of average or repeat all analyses).
- 3.1.7.3.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for antimony, arsenic, barium, beryllium, cadmium, copper, chromium, lead, nickel, manganese, mercury, phosphorus, selenium, silver, thallium, and zinc. All samples should be analyzed in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the method of standard additions. A quality control sample should be analyzed to check the accuracy of the calibration standards. The results must be within 10% or the calibration repeated.
- 3.1.7.3.3 Cold Vapor AAS Analysis for Mercury. All samples should be analyzed in duplicate. A quality control sample should be analyzed to check the accuracy of the calibration standards (within 15% or repeat

calibration). Perform a matrix spike on one sample from the nitric impinger portion (must be within 25% or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA <u>SW-846</u> Method 7470 or in <u>Standard Methods for the Examination of Water and Wastewater</u>, 15th Edition, Method 303F.

#### 3.1.8 <u>Calculations</u>

- 3.1.8.1 Dry Gas Volume. Using the data from this test, calculate  $V_{m(atd)}$ , the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method.5.
- 3.1.8.2 Volume of Water Vapor and Moisture Content. Using the data obtained from this test, calculate the volume of water vapor  $V_{w(std)}$  and the moisture content  $B_{ws}$  of the stack gas. Use Equations 5-2 and 5-3 of Method 5.
- 3.1.8.3 Stack Gas Velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity.
  - 3.1.8.4 Metals (Except Mercury) in Source Sample.
- 3.1.8.4.1 Fraction 1A, Front Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 1 of the sampling train using the following equation:

$$M_{fh} - C_{a1} F_d V_{soln,1}$$
 Eq. 1\*

where:

 $M_{fh}$  = total mass of each metal (except Hg) collected in the front half of the sampling train (Fraction 1),  $\mu g$ .

 $C_{al}$  = concentration of metal in sample Fraction 1A as read from the standard curve ( $\mu g/ml$ ).

<sup>\*</sup>If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.

 $F_d$  - dilution factor ( $F_d$  - the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading  $C_{al}$ . For example, when 2 ml of Fraction 1A are diluted to 10 ml,  $F_d$  - 5).

V<sub>soln,1</sub> - total volume of digested sample solution (Fraction 1),

3.1.8.4.2 Fraction 2A, Back Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation:

$$M_{bh} = C_{a2}F_aV_a \qquad Eq. 2*$$

where:

 $M_{\rm bh}$  - total mass of each metal (except Hg) collected in the back half of the sampling train (Fraction 2),  $\mu$ g.

 $C_{a2}$  - concentration of metal in sample concentrated Fraction 2A, as read from the standard curve ( $\mu g/ml$ ).

F<sub>a</sub> = aliquot factor, volume of Fraction 2 divided by volume of aliquot Fraction 2A (see Section 3.1.5.3.4).

 $V_a$  - total volume of digested sample solution (concentrated Fraction 2A), ml (see Section 3.1.5.3.4.1 or 3.1.5.3.4.2, as applicable).

3.1.8.4.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_{t} = (M_{th} - M_{thb}) + (M_{bh} - M_{bhb})$$
 Eq. 3\*

where:

 $M_t$  - total mass of each metal (separately stated for each metal) collected in the sampling train,  $\mu_g$ .

 $M_{\rm fhb}$  = blank correction value for mass of metal detected in front-half field reagent blank,  $\mu_{\rm g}$ .

 $M_{bhb}$  - blank correction value for mass of metal detected in back-half field reagent blank,  $\mu g$ .

Note: If the measured blank value for the front half  $(m_{fhb})$  is in the range 0.0 to A  $\mu g$  [where A  $\mu g$  equals the value determined by multiplying 1.4  $\mu g$  per square inch  $(1.4 \ \mu g/in^2)$  times the actual area in square inches  $(in^2)$ 

of the filter used in the emission sample],  $m_{fhb}$  may be used to correct the emission sample value  $(m_{fh})$ ; if  $m_{fhb}$  exceeds A  $\mu$ g, the greater of the two following values (either I. or II.) may be used:

- I. A  $\mu$ g, or
- II. the lesser of (a)  $m_{fhb}$ , or (b) 5 percent of  $m_{fh}$ .

If the measured blank value for the back half  $(m_{bhb})$  is in the range of 0.0 to 1  $\mu$ g,  $m_{bhb}$  may be used to correct the emission sample value  $(m_{bh})$ ; if  $m_{bhb}$  exceeds 1  $\mu$ g, the greater of the two following values may be used: 1  $\mu$ g or 5 percent of  $m_{bh}$ .

- 3.1.8.5 Mercury in Source Sample.
- 3.1.8.5.1 Fraction 1B, Front Half, Hg. Calculate the amount of mercury collected in the front half, Fraction 1, of the sampling train using the following equation:

$$Hg_{fh} = \frac{Q_{fh}}{V_{soln,1}} \times V_{soln,1}$$
 Eq. 4

where:

 $Hg_{fh}$  = total mass of mercury collected in the front half of the sampling train (Fraction 1),  $\mu g$ .

 $Q_{fh}$  = quantity of mercury in analyzed sample,  $\mu g$ .

 $V_{soln,1}$  = total volume of digested sample solution (Fraction 1),

 $V_{\text{flB}}$  - volume of Fraction 1B analyzed, ml. See the following notice.

Note:  $V_{f1B}$  is the actual amount of Fraction 1B analyzed. For example, if 1 ml of Fraction 1B were diluted to 100 ml to bring it into the proper analytical range, and 1 ml of the 100-ml dilution were analyzed,  $V_{f1B}$  would be 0.01 ml.

3.1.8.5.2 Fraction 2B and Fractions 3A, 3B, and 3C, Back Half, Hg. Calculate the amount of mercury collected in Fractions 2 using Equation 5 and in Fractions 3A, 3B, and 3C using Equation 6. Calculate the total amount of mercury collected in the back half of the sampling train using Equation 7.

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2R}} \times V_{soln,2}$$
 Eq. 5

where:

 $Hg_{bh2}$  = total mass of mercury collected in Fraction 2,  $\mu g$ .  $Q_{bh2}$  = quantity of mercury in analyzed sample,  $\mu g$ .  $V_{soln,2}$  = total volume of Fraction 2, ml.  $V_{f2B}$  = volume of Fraction 2B analyzed, ml (see the following note).

Note:  $V_{f2B}$  is the actual amount of Fraction 2B analyzed. For example, if 1 ml of Fraction 2B were diluted to 10 ml to bring it into the proper analytical range, and 5 ml of the 10-ml dilution was analyzed,  $V_{f2B}$  would be 0.5.

Use Equation 6 to calculate separately the back-half mercury for Fractions 3A, then 3B, then 3C.

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}} \times V_{soln,3(A,B,C)}$$
 Eq. 6

where:

Hg<sub>bh3(A,B,C)</sub> = total mass of mercury collected separately in Fraction 3A, 3B, or 3C,  $\mu$ g.

Q<sub>bh3(A,B,C)</sub> = quantity of mercury in separately analyzed samples,  $\mu$ g.

 $V_{f3(A,B,C)}$  = volume of Fraction 3A, 3B, or 3C analyzed, ml (see Note in Sections 3.1.8.5.1 and 3.1.8.5.2, and calculate similarly).

 $V_{soln,3(A,B,C)}$  = total volume of Fraction 3A, 3B, or 3C, m1.

$$Hg_{bh} - Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C}$$
 Eq. 7

where:

 $Hg_{bh}$  = total mass of mercury collected in the back half of the sampling train,  $\mu g$ .

3.1.8.5.3 Total Train Mercury Catch. Calculate the total amount of mercury collected in the sampling train using Equation 8.

$$Hg_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb})$$
 Eq. 8

where:

 $Hg_t$  = total mass of mercury collected in the sampling train,  $\mu g$ .

 $Hg_{fhb}$  = blank correction value for mass of mercury detected in front-half field reagent blank,  $\mu g$ .

 $Hg_{bhb}$  = blank correction value for mass of mercury detected in back-half field reagent blanks,  $\mu g$ .

Note: If the total of the measured blank values ( $Hg_{fhb}$  +  $Hg_{bhb}$ ) is in the range of 0 to 6  $\mu g$ , then the total may be used to correct the emission sample value ( $Hg_{fh}$  +  $Hg_{bh}$ ); if it exceeds 6  $\mu g$ , the greater of the following two values may be used; 6  $\mu g$  or 5 percent of the emission sample value ( $Hg_{fh}$  +  $Hg_{bh}$ ).

3.1.8.6 Metal Concentration of Stack Gas. Calculate each metal separately for the cadmium, total chromium, arsenic, nickel, manganese, beryllium, copper, lead, phosphorus, thallium, silver, barium, zinc, selenium, antimony, and mercury concentrations in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_4(M_t/V_{m(std)})$$
 Eq. 9

where:

 $C_s$  = concentration of each metal in the stack gas, mg/dscm.

 $K_4 = 10^{-3} \text{ mg/}\mu\text{g}.$ 

 $M_t$  = total mass of each metal collected in the sampling train,  $\mu g$ ; (substitute  $Hg_t$  for  $M_t$  for the mercury calculation).

 $V_{m(std)}$  - volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

3.1.8.7 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively.

# 3.1.9 <u>Bibliography</u>

- 3.1.9.1 Method 303F in <u>Standard Methods for the Examination of Water and Wastewater</u>, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street, N.W., Washington, D.C. 20036.
- 3.1.9.2 EPA Methods 6010, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C. 20460.
- 3.1.9.3 EPA Method 200.7, <u>Code of Federal Regulations</u>, Title 40, Part 136, Appendix C. July 1, 1987.
- 3.1.9.4 EPA Methods 1 through 5, and 12 <u>Code of Federal Regulations</u>, Title 40, Part 60, Appendix A, July 1, 1987.

# 3.2 <u>Determination of Hexavalent Chromium Emissions from Stationary</u> Sources (Method Cr<sup>+6</sup>)

#### 3.2.1 Applicability and Principle

- 3.2.1.1 Applicability. This method applies to the determination of hexavalent chromium ( $Cr^{+6}$ ) emissions from hazardous waste incinerators, municipal waste combustors, sewage sludge incinerators, and boilers and industrial furances. With the approval of the Administrator, this method may also be used to measure total chromium. The sampling train, constructed of Teflon components, has only been evaluated at temperatures less than  $300^{\circ}F$ . Trains constructed of other materials, for testing at higher temperatures, are currently being evaluated.
- 3.2.1.2 Principle. For incinerators and combustors, the Cr<sup>+6</sup> emissions are collected isokinetically from the source. To eliminate the possibility of Cr<sup>+6</sup> reduction between the nozzle and impinger, the emission samples are collected with a recirculatory train where the impinger reagent is continuously recirculated to the nozzle. Recovery procedures include a post-sampling purge and filtration. The impinger train samples are analyzed for Cr<sup>+6</sup> by an ion chromatograph equipped with a post-column reactor and a visible wavelength detector. The IC/PCR separates the Cr<sup>+6</sup> as chromate (CrO<sub>4</sub><sup>\*</sup>) from other components in the sample matrices that may interfere with the Cr<sup>+6</sup>-specific diphenylcarbazide reaction that occurs in the post-column reactor. To increase sensitivity for trace levels of chromium, a preconcentration system is also used in conjunction with the IC/PCR.

# 3.2.2 Range, Sensitivity, Precision, and Interference

3.2.2.1 Range. Employing a preconcentration procedure, the lower limit of the detection range can be extended to 16 nanograms per dry standard cubic meter (ng/dscm) with a 3 dscm gas sample (0.1 ppb in solution). With sample dilution, there is no upper limit.

- 3.2.2.2 Sensitivity. A minimum detection limit of 8 ng/dscm with a 3 dscm gas sample can be achieved by preconcentration (0.05 ppb in solution).
- 3.2.2.3 Precision. The precision of the IC/PCR with sample preconcentration is 5 to 10 percent. The overall precision for sewage sludge incinerators emitting 120 ng/dscm of  $Cr^{+6}$  and  $3.5~\mu g/dscm$  of total chromium is 25% and 9% for  $Cr^{+6}$  and total chromium, respectively; for hazardous waste incinerators emitting 300 ng/dscm of  $Cr^{+6}$  it is 20 percent.
- 3.2.2.4 Interference. Components in the sample matrix may cause  $Cr^{+6}$  to convert to trivalent chromium  $(Cr^{+3})$  or cause  $Cr^{+3}$  to convert to  $Cr^{+6}$ . A post-sampling nitrogen purge and sample filtration are included to eliminate many of these interferences. The chromatographic separation of  $Cr^{+6}$  using ion chromatography reduces the potential for other metals to interfere with the post-column reaction. For the IC/PCR analysis, only compounds that coelute with  $Cr^{+6}$  and affect the diphenylcarbazide reaction will cause interference. Periodic analysis of deionized (DI) water blanks is used to demonstrate that the analytical system is essentially free from contamination. Sample cross-contamination that can occur when high-level and low-level samples or standards are analyzed alternately is eliminated by thorough purging of the sample loop. Purging can easily be achieved by increasing the injection volume of the samples to ten times the size of the sample loop.

#### 3.2.3 Apparatus

3.2.3.1 Sampling Train. Schematics of the recirculating sampling trains employed in this method are shown in Figures 3.2-1 and 3.2-2. The recirculatory train is readily assembled from commercially available components. All portions of the train in contact with the sample are either glass, quartz, Tygon, or Teflon, and are to be cleaned as per subsection 3.2.5.1.1.

The metering system is identical to that specified by Method 5 (see Section 3.8.1); the sampling train consists of the following components:

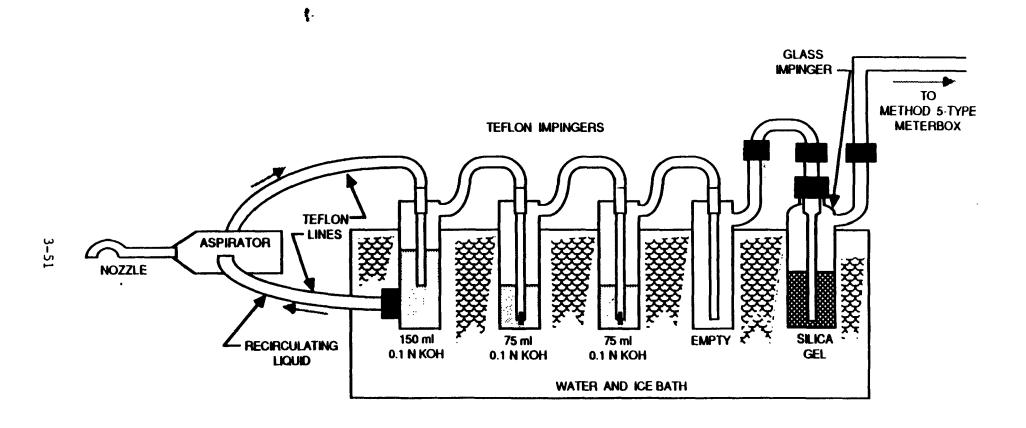


Figure 3.2-1 Schematic of recirculatory impinger train with aspirator assembly.

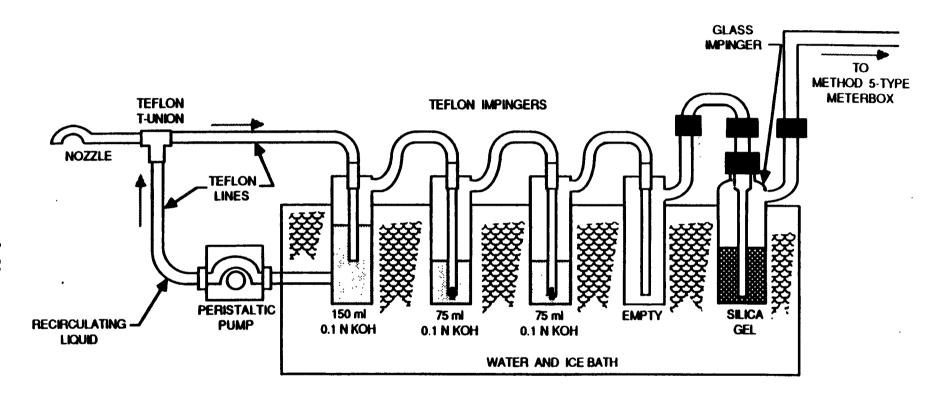


Figure 3.2-2

3.2.3.1.1 Probe Nozzle. Glass or Teflon with a sharp, tapered leading edge. The angle of taper shall be  $\leq 30^{\circ}$  and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in) (or larger if higher volume sample trains are used) inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in). Each nozzle shall be calibrated according to the procedures outlined in Section 3.2.6.

- 3.2.3.1.2 Teflon Aspirator or Pump/Sprayer Assembly. Teflon aspirator capable of recirculating absorbing reagent at 50 ml/min while operating at 0.75 cfm. Alternatively, a pump/sprayer assembly may be used instead of the Teflon aspirator. A Teflon union-T is connected behind the nozzle to provide the absorbing reagent/sample gas mix; a peristaltic pump is used to recirculate the absorbing reagent at a flow rate of at least 50 ml/min. Teflon fittings, Teflon ferrules, and Teflon nuts are used to connect a glass or Teflon nozzle, recirculating line, and sample line to the Teflon aspirator or union-T. Tygon, C-flex\*\* or other suitable inert tubing for use with peristaltic pump.
- 3.2.3.1.3 Teflon Sample Line. Teflon, 3/8" outside diameter (OD) and 1/4" inside diameter (ID), or 1/2" OD x 3/8" ID, of suitable length to connect aspirator (or T-union) to first Teflon impinger.
- 3.2.3.1.4 Teflon Recirculation Line. Teflon, 1/4" 0.D. and 1/8" I.D., of suitable length to connect first impinger to aspirator (or T-union).
- 3.2.3.1.5 Teflon Impingers. Four Teflon Impingers; Teflon tubes and fittings, such as made by Savillex\*\*, can be used to construct impingers

<sup>\*\*</sup>NOTE: Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

- 2" diameter by 12" long, with vacuum-tight 3/8" O.D. Teflon compression fittings. Alternatively, standard glass impingers that have been Teflon-lined, with Teflon stems and U-tubes, may be used. Inlet fittings on impinger top to be bored through to accept 3/8" O.D. tubing as impinger stem. The second and third 3/8" OD Teflon stem has a 1/4" OD Teflon tube, 2" long, inserted at its end to duplicate the effects of the Greenburg-Smith impinger stem. The first impinger stem should extend 2" from impinger bottom, high enough in the impinger reagent to prevent air from entering recirculating line; the second and third impinger stems should extent to 1/2" from impinger bottom. The first impinger should include a 1/4" O.D. Teflon compression fitting for recirculation line. The fourth impinger serves as a knockout impinger.
- 3.2.3.1.6 Glass Impinger. Silica gel impinger. Vacuum-tight impingers, capable of containing 400 g of silica gel, with compatible fittings. The silica gel impinger will have a modified stem (1/2" ID at tip of stem).
- 3.2.3.1.7 Thermometer, (identical to that specified by Method 5) at the outlet of the silica gel impinger, to monitor the exit temperature of the gas.
- 3.2.3.1.8 Metering System, Barometer, and Gas Density Determinations Equipment. Same as Method 5, Sections 2.1.8 through 2.1.10, respectively.
- 3.2.3.2 Sample Recovery. Clean all items for sample handling or storage with 10% nitric acid solution by soaking, where possible, and rinse thoroughly with DI water before use.
- 3.2.3.2.1 Nitrogen Purge Line. Inert tubing and fittings capable of delivering 0 to 1 scf/min (continuously adjustable) of nitrogen gas to the impinger train from a standard gas cylinder (see Figure  $\frac{Cr^{+6}-3}{2}$ ). Standard 3/8-inch Teflon tubing and compression fittings in conjunction with an adjustable pressure regulator and needle valve may be used.

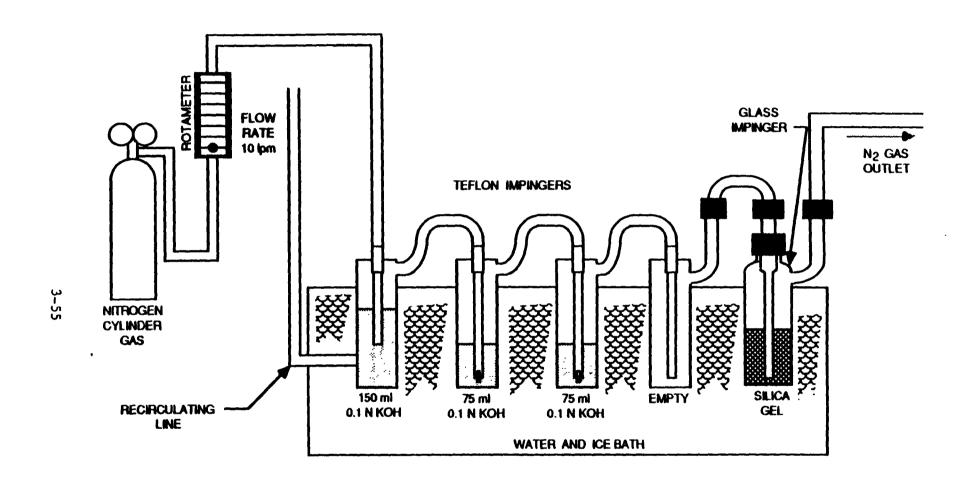


Figure 3.2-3
Schematic of post test nitrogen purge system

- 2.3.2.2 Wash Bottles. Two polyethylene wash bottles, for DI water and atric rinse solution.
- 3.2.3.2.3 Sample Storage Containers. Polyethylene, with leak-free screw cap, 500-ml or 1000-ml.
  - 3.2.3.2.4 1000-ml Graduated Cylinder.
- 3.2.3.2.5 Plastic Storage Containers. Air tight containers to store silica gel.
- 3.2.3.2.6 Funnel and Rubber Policeman. To aid in transfer of silica gel from impinger to storage container; not necessary if silica gel is weighed directly in the impinger.

#### 3.2.3.2.7 Balance

- 3.2.3.3 Sample Preparation for Analysis. Sample preparation prior to analysis includes purging the sample train immediately following the sample run, and filtering the recovered sample to remove particulate matter immediately following recovery.
- 3.2.3.3.1 Beakers, Funnels, Volumetric Flasks, Volumetric Pipets, and Graduated Cylinders. Assorted sizes, Teflon or glass, for preparation of samples, sample dilution, and preparation of calibration standards. Prepare initially following procedure described in Section 3.2.5.1.3 and rinse between use with 0.1 N HNO<sub>3</sub> and DI water.
- 3.2.3.3.2 Filtration Apparatus. Teflon, or equivalent, for filtering samples, and Teflon filter holder. Teflon impinger components have been found to be satisfactory as a sample reservoir for pressure filtration using nitrogen.

## 3.2.3.4 Analysis.

- 3.2.3.4.1 IC/PCR System. High performance liquid chromatograph pump, sample injection valve, post-column reagent delivery and mixing system, and a visible detector, capable of operating at 520 nm, all with a non-metallic (or inert) flow path. An electronic recording integrator operating in the peak area mode is recommended, but other recording devices and integration techniques are acceptable provided the repeatability criteria and the linearity criteria for the calibration curve described in Section 3.2.5.5 can be satisfied. A sample loading system will be required if preconcentration is employed.
- 3.2.3.4.2 Analytical Column. A high performance ion chromatograph (HPIC) non-metallic column with anion separation characteristics and a high loading capacity designed for separation of metal chelating compounds to prevent metal interference. Resolution described in Section 3.2.5.4 must be obtained. A non-metallic guard column with the same ion-exchange material is recommended.
- 3.2.3.4.3 Preconcentration Column. An HPIC non-metallic column with acceptable anion retention characteristics and sample loading rates as described in Section 3.2.5.5.
- 3.2.3.4.4 0.45 um filter cartridge. For the removal of insoluble material. To be used just prior to sample injection/analysis.

## 3.2.4 Reagents

All reagents should, at a minimum, conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. All prepared reagents should be checked by IC/PCR analysis for Cr<sup>+6</sup> to ensure that contamination is below the analytical detection limit for direct injection or, if selected, preconcentration. If total chromium is also to be determined, the reagents

should also be checked by the analytical technique selected to ensure that contamination is below the analytical detection limit.

- 3.2.4.1 Sampling.
- 3.2.4.1.1 Water. Deionized water. It is recommended that water blanks be checked prior to preparing sampling reagents to ensure that the  $\rm Cr^{+6}$  content is less than the analytical detection limit.
- 3.2.4.1.2 Potassium Hýdroxide, 0.1 N. Add 5.6 gm of KOH(s) to approximately 900 ml of DI water and let dissolve. Dilute to 1000 ml with DI water. NOTE: At sources with high concentrations of acids and/or  $SO_2$ , the concentration of KOH should be increased to 0.5 N to ensure that the pH of the solution is above 8.5 after sampling.
- 3.2.4.1.3 Silica Gel and Crushed Ice. Same as Method 5, Sections 3.1.2 and 3.1.4, respectively.
- 3.2.4.2 Sample Recovery. The reagents used in sample recovery are as follows:
  - 3.2.4.2.1 Water. Same as Subsection 3.2.4.1.1.
- 3.2.4.2.2 Nitric Acid, 0.1 N. Add 6.3 ml of concentrated  $\mathrm{HNO_3}$  (70 percent) to a graduated cylinder containing approximately 900 ml of DI water. Dilute to 1000 ml with DI water, and mix well.
- 3.2.4.2.3 pH Indicator Strip. pH indicator capable of determining pH of solution between the pH range of 7 and 12, at 0.5 pH intervals.
  - 3.2.4.3 Sample Preparation
  - 3.2.4.3.1 Water. Same as Subsection 3.2.4.1.1.
  - 3.2.4.3.2 Nitric Acid, 0.1 N. Same as Subsection 3.2.4.2.2.

3.2.4.3.3 Filters. Acetate membrane, or equivalent, filters with 0.45 micrometer or smaller pore size to remove insoluble material.

## 3.2.4.4 Analysis.

- 3.2.4.4.1 Chromatographic Eluent. The eluent used in the analytical system is ammonium sulfate based. It is prepared by adding 6.5 ml of 29 percent ammonium hydroxide (NH<sub>4</sub>OH) and 33 grams of ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] to 500 ml of DI water. The mixture should then be diluted to 1 liter with DI water and mixed well. Other combinations of eluents and/or columns may be employed provided peak resolution, as described in Section 3.2.5.4, repeatability and linearity, as described in Section 3.2.6.2, and analytical sensitivity are acceptable.
- 3.2.4.4.2 Post-Column Reagent. An effective post-column reagent for use with the chromatographic eluent described in Section 3.2.4.4.1 is a diphenylcarbazide (DPC) based system. Dissolve 0.5 g of 1,5-diphenylcarbazide (DPC) in 100 ml of ACS grade methanol. Add to 500 ml of degassed DI water containing 50 ml of 96 percent spectrophotometric grade sulfuric acid. Dilute to 1 liter with degassed DI water.
- 3.2.4.4.3 Cr<sup>+6</sup> Calibration Standard. Prepare Cr<sup>+6</sup> standards from potassium dichromate ( $K_2$ Cr<sub>2</sub>O<sub>7</sub>, FW 294.19). To prepare a 1000  $\mu$ g/ml Cr<sup>+6</sup> stock solution, dissolve 2.829 g of dry  $K_2$ Cr<sub>2</sub>O<sub>7</sub> in 1 liter of DI water. To prepare working standards, dilute the stock solution to the chosen standard concentrations for instrument calibration with 0.05 N KOH to achieve a matrix similar to the actual field samples.
- 3.2.4.4.4 Performance Audit Sample. A performance audit sample shall be obtained from the Quality Assurance Division of EPA and analyzed with the field samples. The mailing address to request audit samples is:

U.S. Environmental Protection Agency Atmospheric Research and Exposure Assessment Laboratory Quality Assurance Division Source Branch, Mail Drop 77-A Research Triangle Park, North Carolina 27711

The audit sample should be prepared in a suitable sample matrix at a concentration similar to the actual field samples.

## 3.2.5 Procedure

SAFETY FIRST - WEAR SAFETY GLASSES AT ALL TIMES DURING THIS TEST METHOD.

- 3.2.5.1 Sampling. The complexity of this method is such that to obtain reliable results, testers should be trained and experienced with test procedures.
- 3.2.5.1.1 Pretest Preparation. All components shall be maintained and calibrated according to the procedures described in APTD-0576, unless otherwise specified herein.

Rinse all sample train components from the glass nozzle up to the silica gel impinger and sample containers with hot tap water followed by washing with hot soapy water. Next, rinse the train components and sample containers three times with tap water followed by three rinses with DI water. All the components and containers should then be soaked overnight, or a minimum of 4 hours, in a 10 percent (v/v) nitric acid solution, then rinsed three times with DI water. Allow the components to air dry prior to covering all openings with Parafilm, or equivalent.

- 3.2.5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.
- 3.2.5.1.3 Preparation of Sampling Train. Measure 300 ml of 0.1 N KOH into a graduated cylinder (or tare-weighed precleaned polyethylene

container). Place approximately 150 ml of the 0.1 N KOH reagent in the first Teflon impinger. Split the rest of the 0.1 N KOH between the second and third Teflon impingers. The next Teflon impinger is left dry. Place a preweighed 200- to 400-g portion of indicating silica gel in the final glass impinger. (For sampling periods in excess of two hours, or for high moisture sites, 400-g of silica gel is recommended.)

Retain reagent blanks of the  $0.1\ N$  KOH equal to the volumes used with the field samples.

- 3.2.5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).
- 3.2.5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. The sampling train should be iced down with water and ice to ensure heat transfer with the Teflon impingers.

NOTE: If the gas to be sampled is above 200°F, it may be necessary to wrap three or four feet of the Teflon sample and recirculating lines inside the ice bath to keep the recirculated reagent cool enough so it does not turn to steam.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

At the end of the sampling run, determine the pH of the reagent in the first impinger using a pH indicator strip. The pH of the solution shall be greater than 8.5.

3.2.5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

3.2.5.2 Post-Test Nitrogen Purge. The nitrogen purge is used as a safeguard against the conversion of hexavalent chromium to the trivalent oxidation state. The purge is effective in the removal of  $SO_2$  from the impinger contents.

Attach the nitrogen purge line to the input of the impinger train. Check to ensure the output of the impinger train is open, and that the recirculating line is capped off. Open the nitrogen gas flow slowly and adjust the delivery rate to 10 L/min. Check the recirculating line to ensure that the pressure is not forcing the impinger reagent out through this line. Continue the purge under these conditions for one-half hour, periodically checking the flow rate.

3.2.5.3 Sample Recovery. Begin cleanup procedures as soon as the train assembly has been purged at the end of the sampling run. The probe assembly may be disconnected from the sample train prior to sample purging.

The probe assembly should be allowed to cool prior to sample recovery. Disconnect the umbilical cord from the sample train. When the probe assembly can be safely handled, wipe off all external particulate matter near the tip of the nozzle, and cap the nozzle prior to transporting the sample train to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions.

3.2.5.3.1 Container No. 1 (Impingers 1 through 3). Disconnect the first impinger from the second impinger and disconnect the recirculation line from the aspirator or peristaltic pump. Drain the Teflon impingers into a precleaned graduated cylinder or tare-weighed precleaned polyethylene sample container and measure the volume of the liquid to within 1 ml or 1 g. Record the volume of liquid present as this information is required to calculate the moisture content of the flue gas sample. If necessary, transfer the sample from the graduated cylinder to a precleaned polyethylene sample container. With DI water, rinse four times the insides of the glass nozzle, the aspirator, the sample and recirculation lines, the impingers, and the connecting

tubing, and combine the rinses with the impinger solution in the sample container.

- 3.2.5.3.2 Container No. 2 (HNO $_3$  rinse optional for total chromium). With 0.1 N HNO $_3$ , rinse three times the entire train assembly, from the nozzle to the fourth impinger and combine the rinses into a separate precleaned polyethylene sample container for possible total chromium analysis. Repeat the rinse procedure a final time with DI water, and discard the water rinses. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.
- 3.2.5.3.3 Container No. 3 (Silica Gel). Note the color of the indicating silica gel to determine if it has been completely spent. Quantitatively transfer the silica gel from its impinger to the original container, and seal the container. A funnel and a rubber policeman may be used to aid in the transfer. The small amount of particulate that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or the silica gel plus impinger) to the nearest 0.5 g.
- 3.2.5.3.4 Container No. 4 (0.1 N KOH Blank). Once during each field test, place a volume of reagent equal to the volume placed in the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.
- 3.2.5.3.5 Container No. 5 (DI Water Blank). Once during each field test, place a volume of DI water equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alterna-

tively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

- 3.2.5.3.6 Container No. 6 (0.1 N HNO<sub>3</sub> Blank). Once during each field test if total chromium is to be determined, place a volume of 0.1 N HNO<sub>3</sub> reagent equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.
- 3.2.5.4 Sample Preparation. For determination of  $Cr^{+6}$ , the sample should be filtered <u>immediately following recovery</u> to remove any insoluble matter. Nitrogen gas may be used as a pressure assist to the filtration process (see Figure  $Cr^{+6}$ -4).

Filter the entire impinger sample through a 0.45-micrometer acetate filter (or equivalent), and collect the filtrate in a 1000-ml graduated cylinder. Rinse the sample container with DI water three separate times, pass these rinses through the filter, and add the rinses to the sample filtrate. Rinse the Teflon reservoir with DI water three separate times, pass these rinses through the filter, and add the rinses to the sample. Determine the final volume of the filtrate and rinses and return them to the rinsed polyethylene sample container. Label the container clearly to identify its contents. Rinse the Teflon reservoir once with 0.1 N HNO<sub>3</sub> and once with DI water and discard these rinses.

If total chromium is to be determined, quantitatively recover the filter and residue and place them in a vial. (The acetate filter may be digested with 5 ml of 70 percent nitric acid; this digestion solution may then be diluted with DI water for total chromium analysis.)

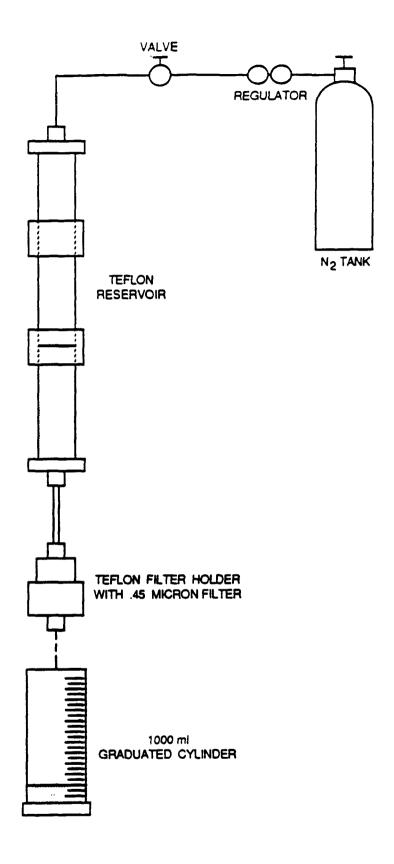


Figure 3.2-4 Schematic of sample filter system.

NOTE: If the source has a large amount of particulate in the effluent stream, testing teams may wish to filter the sample twice, once through a 2 to 5-micrometer filter, and then through the 0.45-micrometer filter.

- 3.2.5.4.1 Container 2 (HNO<sub>3</sub> rinse, optional for total chromium). This sample shall be analyzed in accordance with the selected procedure for total chromium analysis. At a minimum, the sample should be subjected to a digestion procedure sufficient to solubilize all chromium present.
- 3.2.5.4.2 Container 3 (Silica Gel). Weigh the spent silica gel to the nearest 0.5 g using a balance. (This step may be conducted in the field.)
- 3.2.5.5 Sample analysis. The Cr<sup>+6</sup> content of the sample filtrate is determined by ion chromatography coupled with a post-column reactor (IC/PCR). To increase sensitivity for trace levels of chromium, a preconcentration system is also used in conjunction with the IC/PCR.

Prior to preconcentration and/or analysis, all field samples will be filtered through a  $0.45-\mu$  filter. This filtration should be conducted just prior to sample injection/analysis.

The preconcentration is accomplished by selectively retaining the analyte on a solid absorbent (as described in 3.2.3.4.3), followed by removal of the analyte from the absorbent. The sample is injected into a sample loop of the desired size (repeated loadings or larger size loop for greater sensitivity) and the Cr<sup>+6</sup> is collected on the resin bed of the column. When the injection valve is switched, the eluent displaces the concentrated Cr<sup>+6</sup> sample moving it off the preconcentration column and onto the IC anion separation column. After separation from other sample components, Cr<sup>+6</sup> forms a specific complex in the post-column reactor with a diphenylcarbazide reaction solution, and the complex is then detected by visible absorbance at a wavelength of 520 nm. The amount of absorbance measured is proportional to the concentration of the Cr<sup>+6</sup> complex formed. The IC retention time and absorbance of the Cr<sup>+6</sup> complex is compared with known Cr<sup>+6</sup> standards analyzed

under identical conditions to provide both qualitative and quantitative analyses.

Prior to sample analysis, establish a stable baseline with the detector set at the required attenuation by setting the eluent flowrate at approximately 1 ml/min and post-column reagent flowrate at approximately 0.5 ml/min. (Note: As long as the ratio of eluent flowrate to PCR flowrate remains constant, the standard curve should remain linear.) Inject a sample of DI water to ensure that no  $Cr^{+6}$  appears in the water blank.

First, inject the calibration standards prepared, as described in Section 3.2.4.4.4, to cover the appropriate concentration range, starting with the lowest standard first. Next, inject, in duplicate, the performance audit sample, followed by the 0.1 N KOH field blank and the field samples. Finally, repeat the injection of the calibration standards to allow for compensation of instrument drift. Measure areas or heights of the Cr<sup>+6</sup>/DPC complex chromatogram peak. The response for replicate, consecutive injections of samples must be within 5 percent of the average response, or the injection should be repeated until the 5 percent criterion can be met. Use the average response (peak areas or heights) from the duplicate injections of calibration standards to generate a linear calibration curve. From the calibration curve, determine the concentration of the field samples employing the average response from the duplicate injections.

The results for the analysis of the performance audit sample must be within 10 percent of the reference value for the field sample analysis to be valid.

- 3.2.6 <u>Calibration</u>. Maintain a written log of all calibration activities.
- 3.2.6.1 Sample Train Calibration. Calibrate the sample train components according to the indicated sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

3.2.6.2 Calibration Curve for the IC/PCR. Prepare working standards from the stock solution described in Section 3.2.4.4.4 by dilution with a DI water solution to approximate the field sample matrix. Prepare at least four standards to cover one order of magnitude that bracket the field sample concentrations. Run the standards with the field samples as described in Section 3.2.5.5. For each standard, determine the peak areas (recommended) or the peak heights, calculate the average response from the duplicate injections, and plot the average response against the  ${\rm Cr}^{+6}$  concentration in  $\mu {\rm g/L}$ . The individual responses for each calibration standard determined before and after field sample analysis must be within 5 percent of the average response for the analysis to be valid. If the 5 percent criteria is exceeded, excessive drift and/or instrument degradation may have occurred, and must be corrected before further analyses are performed.

Employing linear regression, calculate a predicted value for each calibration standard with the average response for the duplicate injections. Each predicted value must be within 7 percent of the actual value for the calibration curve to be considered acceptable. If not acceptable, remake and/or rerun the calibration standards. If the calibration curve is still unacceptable, reduce the range of the curve.

## 3.2.7 <u>Calculations</u>

- 3.2.7.1 Dry Gas Volume. Using the data from the test, calculate  $V_{m(std)}$ , the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.
- 3.2.7.2 Volume of Water Vapor and Moisture Content. Using the data from the test, calculate  $V_{w(std)}$  and  $B_{ws}$ , the volume of water vapor and the moisture content of the stack gas, respectively, using Equations 5-2 and 5-3 of Method 5.
- 3.2.7.3 Stack Gas Velocity. Using the data from the test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

3.2.7.4 Total  $\mu$ g Cr<sup>+6</sup> per Sample. Calculate as described below:

$$m = (S-B) \times V_{1s} \times d$$

## where:

m = Mass of  $Cr^{+6}$  in the sample,  $\mu g$ . S = Concentration of sample,  $\mu g Cr^{+6}/ml$ . B = Concentration of blank,  $\mu g Cr^{+6}/ml$ .  $V_{1s}$  = Volume of sample after filtration, ml. d = Dilution factor (1 if not diluted).

# 3.3 <u>Measurement of HCl and Cl</u><sub>2</sub>

# 3.3.1 <u>Isokinetic HCl/Cl<sub>2</sub> Emission Sampling Train (Method 0050)</u>

### 3.3.1.1 Scope and Application

- 3.3.1.1.1 This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl<sub>2</sub>, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators, municipal waste combustors, and boilers and industrial furnaces. The collected samples are analyzed using Method 9057. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (e.g., HCl dissolved in water droplets). A midget impinger train sampling method designed for sampling sources of HCl/Cl<sub>2</sub> emissions not in particulate form is presented in Method 0051.
- 3.3.1.1.2 This method is not acceptable for demonstrating compliance with HCl emission standards less than 20 ppm.
- 3.3.1.1.3 This method may also be used to collect samples for subsequent determination of particulate emissions (by EPA Method 5, Reference 1) following the additional sampling procedures described.

## 3.3.1.2 Summary of Method

3.3.1.2.1 Gaseous and particulate pollutants are withdrawn from an emission source and are collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain liquid droplets. The Teflon mat or quartz-fiber filter collects other particulate matter including chloride salts. Acidic and alkaline absorbing solutions collect gaseous HCl and  $\text{Cl}_2$ , respectively. Following sampling of emissions containing liquid droplets, any  $\text{HCl/Cl}_2$  dissolved in the liquid in the cyclone and/or on the filter is vaporized and ultimately collected in the impingers by pulling

Ascarite II<sup>R</sup> conditioned ambient air through the sampling train. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride (Cl<sup>-</sup>) ions. The Cl<sub>2</sub> gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H<sup>+</sup>), Cl-, and hypochlorous acid (HClO). The Cl<sup>-</sup> ions in the separate solutions are measured by ion chromatography (Method 9057). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in EPA Method 5 (Reference 1).

### 3.3.1.3 Interferences

3.3.1.3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine (Cl<sub>2</sub>) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl<sub>2</sub> gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present.

## 3.3.1.4 Apparatus and Materials

## 3.3.1.4.1 Sampling Train

3.3.1.4.1.1 A schematic of the sampling train used in this method is shown in Figure 3.3-1. This sampling train configuration is adapted from EPA Method 5 procedures, and, as such, the majority of the required equipment is identical to that used in EPA Method 5 determinations. The new components required are a glass nozzle and probe, a Teflon union, a quartz-fiber or Teflon mat filter (see Section 3.3.1.5.5), a Teflon frit, and acidic and alkaline absorbing solutions.

3.3.1.4.1.2 Construction details for the basic train components are provided in Section 3.4 of EPA's Quality Assurance Handbook, Volume III (Reference 2); commercial models of this equipment are also available.

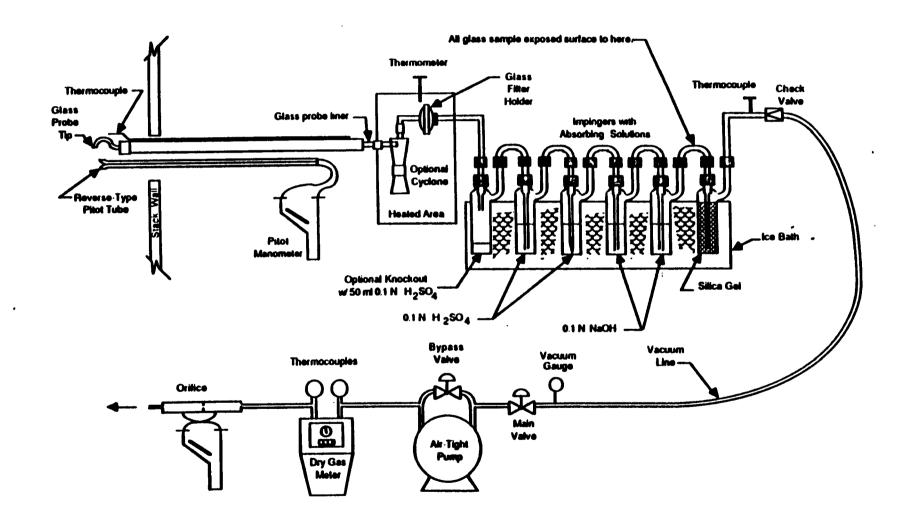


Figure 3.3-1 Isokinetic HC1/C1<sub>2</sub> Sampling Train

Additionally, the following subsections identify allowable train configuration modifications.

- 3.3.1.4.1.3 Basic operating and maintenance procedures for the sampling train are also described in Reference 2. As correct usage is important in obtaining valid results, all users should refer to Reference 2 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.
- 3.3.1.4.1.3.1 Probe nozzle. Glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant I.D. The nozzle shall be buttonhook or elbow design. The nozzle should be coupled to the probe liner using a Teflon union. It is recommended that a stainless steel nut be used on this union. In cases where the stack temperature exceeds 210°C (410°F), a one-piece glass nozzle/liner assembly must be used. A range of nozzle sizes suitable for isokinetic sampling should be available. Each nozzle shall be calibrated according to the procedures outlined in EPA Method 5 (see References 1 and 2).
- 3.3.1.4.1.3.2 Probe liner. Borosilicate or quartz-glass tubing with a heated system capable of maintaining a gas temperature of  $120 \pm 14^{\circ}\text{C}$  ( $248 \pm 25^{\circ}\text{F}$ ) at the exit end during sampling. Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed and calibrated according to the procedure in Reference 2 are considered acceptable. Either borosilicate or quartz-glass probe liners may be used for stack temperatures up to about  $480^{\circ}\text{C}$  ( $900^{\circ}\text{F}$ ). Quartz liners shall be used for temperatures between 480 and  $900^{\circ}\text{C}$  (900 and  $1650^{\circ}\text{F}$ ). (The softening temperature for borosilicate is  $820^{\circ}\text{C}$  ( $1508^{\circ}\text{F}$ ), and for quartz is  $1500^{\circ}\text{C}$  ( $2732^{\circ}\text{F}$ ).) Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding  $500^{\circ}\text{C}$ .
- 3.3.1.4.1.3.3 Pitot tube. Type S, as described in Section 2.1 of EPA Method 2 (Reference 1). The pitot tube shall be attached to the probe to allow constant monitoring of the stack-gas velocity. The impact

(high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Section 3.1.1 of Reference 2) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 3.1.1 of Reference 2.

- 3.3.1.4.1.3.4 Differential pressure gauge. Inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2 (Reference 1). One manometer shall be used for velocity-head (delta P) readings and the other for orifice differential pressure (delta H) readings.
  - 3.3.1.4.1.3.5 Cyclone (optional). Glass.
- 3.3.1.4.1.3.6 Filter holder. Borosilicate glass, with a Teflon frit filter support and a sealing gasket. The sealing gasket shall be constructed of Teflon or equivalent materials. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone.
- 3.3.1.4.1.3.7 Filter heating system. Any heating system capable of maintaining a temperature of  $120 \pm 14^{\circ}\text{C}$  ( $248 \pm 25^{\circ}\text{F}$ ) around the filter and cyclone during sampling. A temperature gauge capable of measuring temperature to within  $3^{\circ}\text{C}$  ( $5.4^{\circ}\text{F}$ ) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.
- 3.3.1.4.1.3.8 Impinger train. The following system shall be used to determine the stack gas moisture content and to collect HCl and Cl<sub>2</sub>: five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first impinger shown in Figure 1 (knockout or condensate impinger) is optional and is recommended as a water knockout trap for use under test conditions which require such a trap. If used, this impinger should be constructed as described below for the alkaline impingers, but with a shortened stem, and should contain 50 ml of 0.1 N  $_{12}$ SO<sub>4</sub>. The following two impingers (acid impingers which each contain 100 ml of 0.1 N  $_{12}$ SO<sub>4</sub>) shall be of the Greenburg-Smith design with the standard

tip (see Method 5, Paragraph 2.1.7). The next two impingers (alkaline impingers which each contain 100 ml of 0.1 N NaOH) and the last impinger (containing silica gel) shall be of the Greenburg-Smith design modified by replacing the tip with a 1.3-cm (1/2-in) I.D. glass tube extending about 1.3 cm (1/2 in) from the bottom of the impinger (see Method 5, Paragraph 2.1.7). The condensate, acid, and alkaline impingers shall contain known quantities of the appropriate absorbing reagents. The last impinger shall contain a known weight of silica gel or equivalent desiccant.

- 3.3.1.4.1.3.9 Metering system. The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry-gas meter capable of measuring volume to within 1 percent, an orifice meter (rate meter), and related equipment, as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry-gas meter should have a recording capacity of 0-999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems capable of maintaining sampling rates within 10 percent of isokineticity and of determining sample volumes to within 2 percent may be used. The metering system should be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.
- 3.3.1.4.1.3.10 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 300-m (100 ft) elevation increase (vice versa for elevation decrease).
- 3.3.1.4.1.3.11 Gas density determination equipment. Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of EPA Method 2), and gas analyzer, if necessary (as described in EPA Method 3, Reference 1). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the

sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see EPA Method 2, Figure 2-7). As a second alternative, if the stack gas is saturated, the stack temperature may be measured at a single point near the center of the stack.

3.3.1.4.1.3.12 Ascarite tube for conditioning ambient air. Tube tightly packed with approximately 150 g of fresh 8 to 20 mesh Ascarite IIR sodium hydroxide coated silica, or equivalent, to dry and remove acid gases from the ambient air used to remove moisture from the filter and optional cyclone. The inlet and outlet ends of the tube should be packed with at least 1 cm thickness of glass wood or filter material suitable to prevent escape of Ascarite II fines. Fit one end with flexible tubing, etc. to allow connection to probe nozzle.

## 3.3.1.4.2 Sample Recovery.

- 3.3.1.4.2.1 Probe liner. Probe and nozzle brushes; nylon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner and the probe nozzle.
- 3.3.1.4.2.2 Wash bottles. Two. Polyethylene or glass, 500 ml or larger.
- 3.3.1.4.2.3 Glass sample storage containers. Glass, 500- or 1000-ml. Screw-cap liners shall be Teflon and constructed so as to be leak-free. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.
- 3.3.1.4.2.4 Petri dishes. Glass or plastic, sealed around the circumference with Teflon tape, for storage and transport of filter samples.

- 3.3.1.4.2.5 Graduated cylinder and/or balances. To measure condensed water to the nearest 1 ml or 1 g. Graduated cylinders shall have subdivisions not >2 ml. Laboratory triple-beam balances capable of weighing to  $\pm~0.5$  g or better are required.
- 3.3.1.4.2.6 Plastic storage containers. Screw-cap polypropylene or polyethylene containers to store silica gel.
- 3.3.1.4.2.7 Funnel and rubber policeman. To aid in transfer of silica gel to container (not necessary if silica gel is weighed in field).
  - 3.3.1.4.2.8 Funnels. Glass, to aid in sample recovery.

# 3.3.1.5 Reagents

- 3.3.1.5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently higher purity to permit its use without lessening the accuracy of the determination.
- 3.3.1.5.2 ASTM Type II water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. It is advisable to analyze a blank sample of this reagent <u>prior</u> to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values (see Method 9057).
- 3.3.1.5.3 Sulfuric acid  $(0.1\ N)$ ,  $H_2SO_4$ . Used as the HCl absorbing reagent in the impinger train. To prepare 1 L, slowly add 2.80 ml of concentrated  $H_2SO_4$  to about 900 ml of water while stirring, and adjust the final volume to 1 L using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent <u>prior</u> to sampling, since

the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values (see Method 9057).

- 3.3.1.5.4 Sodium hydroxide (0.1 N), NaOH. Used as the  $\text{Cl}_2$  absorbing reagent in the impinger train. To prepare 1 L, dissolve 4.00 g of solid NaOH in about 900 ml of water and adjust the final volume of 1 L using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values (see Method 9057).
- 3.3.1.5.5 Filter. Quartz-fiber or Teflon mat (e.g., Pallflex<sup>R</sup> TX40HI45) filter.
- 3.3.1.5.6 Silica gel. Indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.
- 3.3.1.5.7 Acetone. When using this train for determination of particulate emissions, reagent grade acetone,  $\leq 0.001$  percent residue, in glass bottles is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values ( $\leq 0.001$  percent) shall be used. In no case shall a blank value greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.
- 3.3.1.5.8 Crushed ice. Quantities ranging from 10-50 lbs may be necessary during a sampling run, depending on ambient air temperature.
- 3.3.1.5.9 Stopcock grease. Acetone-insoluble, heat-stable silicone grease may be used, if needed. Silicone grease usage is not necessary if screw-on connectors or Teflon sleeves on ground-glass joints are used.

- 3.3.1.6 Sample Collection, Preservation, and Handling
- 3.3.1.6.1 Sample collection is described in this method. The analytical procedures for HCl and  $\text{Cl}_2$  are described in Method 9057 and for particulate matter in EPA Method 5 (Reference 1).
- 3.3.1.6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

### 3.3.1.7 Procedure

- 3.3.1.7.1 Preparation for Field Test.
- 3.3.1.7.1.1 All sampling equipment shall be maintained and calibrated according to the procedures described in Section 3.4.2 of EPA's Quality Assurance Handbook, Volume III (Reference 2).
- 3.3.1.7.1.2 Weigh several 200- to 300-g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger just prior to train assembly.
- 3.3.1.7.1.3 Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass or plastic Petri dishes) and keep the filters in these containers at all times except during sampling (and weighing for particulate analysis).
- 3.3.1.7.1.4 If a particulate determination will be conducted, desiccate the filters at  $20 \pm 5.6^{\circ}$ C ( $68 \pm 10^{\circ}$ F) and ambient pressure for at least 24 hours, and weigh at intervals of at least 6 hours to a constant weight (i.e., <0.5-mg change from previous weighing), recording results to the nearest 0.1 mg. During each weighing, the filter must not be exposed for more than a 2-min period to the laboratory atmosphere and relative humidity above

50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven-dried at 105°C (220°F) for 2-3 hours, desiccated for 2 hours, and weighed.

- 3.3.1.7.2 Preliminary Field Determinations.
- 3.3.1.7.2.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. It is recommended that a leak-check of the pitot lines (see EPA Method 2, Section 3.1) be performed. Determine the stack-gas moisture content using EPA Method 4 or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in EPA Method 2, Section 3.6. if integrated EPA Method 3 (Reference 1) sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as the sample run.
- 3.3.1.7.2.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2).
- 3.3.1.7.2.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.
- 3.3.1.7.2.4 The total sampling time should be two hours. Allocate the same time to all traverse points defined by EPA Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half min. Size the condensate impinger for the expected moisture catch or be prepared to empty it during the run.

### 3.3.1.7.3 Preparation of Sampling Train

- 3.3.1.7.3.1 Add 50 ml of  $0.1\ N\ H_2SO_4$  to the condensate impinger, if used. Place 100 ml of  $0.1\ N\ H_2SO_4$  in each of the next two impingers. Place 100 ml of  $0.1\ N\ NaOH$  in each of the following two impingers. Finally, transfer approximately 200-300 g of preweighed silica gel from its container to the last impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest  $0.5\ g$  and recorded.
- 3.3.1.7.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) filter (weighed, if particulate matter to be determined) in the filter holder. Be sure that the filter is properly centered and the gasket properly placed to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.
- 3.3.1.7.3.3 To use glass liners, install the selected nozzle using a Viton-A O-ring when stack temperatures are <260°C (500°F) and a woven glass-fiber gasket when temperatures are higher. Other connecting systems utilizing either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.
- 3.3.1.7.3.4 Set up the train as in Figure 3.3-1. A minimal amount of silicone grease may be used on ground glass joints. Connect temperature sensors to the appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.
  - 3.3.1.7.3.5 Place crushed ice around the impingers.

- 3.3.1.7.3.6 Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.
  - 3.3.1.7.4 Leak-Check Procedures.
- 3.3.1.7.4.1 Pretest leak-check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.
- 3.3.1.7.4.1.1 If a Viton-A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380-mm Hg (15-in. Hg) vacuum.
  - NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.
- 3.3.1.7.4.1.2 If a woven glass-fiber gasket is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the cyclone, if used, or the filter holder and pulling a 380-mm Hg (15-in. Hg) vacuum (see NOTE above). Then, connect the probe to the train and leak-check at about 25-mm Hg (1-in. Hg) vacuum; alternatively, leak-check the probe with the rest of the sampling train in one step at 380-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m³/min (0.02 cfm), whichever is less, are unacceptable.
- 3.3.1.7.4.1.3 The following leak-check instructions for the sampling train may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of the bypass valve; this will cause water to back up into the filter holder. If the desired volume is exceeded, either leak-check at this higher vacuum or end the leak-check, as shown below, and start over.

- 3.3.1.7.4.1.4 When the leak-check is completed, first slowly remove the plug from the inlet to the probe, cyclone, or filter holder and immediately turn off the vacuum pump. This prevents the liquid in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the fifth impinger.
- 3.3.1.7.4.2 Leak-checks during sample run. If during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary or a port change is conducted, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be conducted according to the procedure outlined in Section 3.3.1.7.4.1, except that it shall be conducted at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester shall void the sampling run. Immediately after a component change or port change, and before sampling is reinitiated, another leak-check similar to a pre-test leak-check is recommended.
- 3.3.1.7.4.3 Post-test leak-check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done using the same procedures as those with the pre-test leak-check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester shall void the sampling run.

### 3.3.1.7.5 Train Operation.

3.3.1.7.5.1 During the sampling run, maintain an isokinetic sampling rate to within 10 percent of true isokinetic, unless otherwise specified by the Administrator. Maintain a temperature around the filter and (cyclone, if used) of  $120 \pm 14^{\circ}\text{C}$  ( $248 \pm 25^{\circ}\text{F}$ ).

- 3.3.1.7.5.2 For each run, record the data required on a data sheet such as the one shown in Figure 3.3-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made before and after each leak-check, and when sampling is halted. Take other readings required by Figure 3.3-2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.
- 3.3.1.7.5.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are positioned properly. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions using a calculator or a nomograph. Nomographs are designed for use when the Type S pitot tube coefficient is  $0.84 \pm 0.02$  and the stack gas equivalent density (dry molecular weight) is equal to  $29 \pm 4$ . If the stack gas molecular weight and the pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations (see Reference 3).
- 3.3.1.7.5.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack, to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.
- 3.3.1.7.5.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

Plant		Ambient Termperature
Location	Į.	Barometric Pressure
Operator	1	Assumed Moisture X
Date	1	Probe Length, m (ft)
Run No.	[	Nozzle Identification No.
Sample Box No.	]	Average Calibrated Nozzle Diameter, cm (in)
Meter Box No.	1	Probe Heater Setting
Meter H <sup>e</sup>	,	Leak Rate, m <sup>3</sup> /min. (cfm)
C Factor	i	Probe Liner Material
Pitot Tube Coefficient Cp		Static Pressure, mm Hg (in Hg)
•	Schematic of Stack Cross Section	Filter No.

Traverse Point Number	Sampling Line (0) min	Vacuum mm Hg (In. Hg)	Stack Temperature (T <sub>s</sub> ) °C(f)	Velocity Head (P <sub>g</sub> ) mm (in) H <sub>2</sub> O	Pressure Differential Across Orifice Meter mm (H <sub>2</sub> O) (in H <sub>2</sub> O)	Gas Sample Volume <sup>m</sup> 3 (ft <sub>3</sub> )			er iture	Temperature of Gas Leaving Condenser or Last Impinger
							<u> </u>			
						<u> </u>			-	<u> </u>
										-
									<del> </del>	<del> </del>
Total							Avg. A	vg		
Average										

- 3.3.1.7.5.6 Traverse the stack cross section, as required by EPA Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.
- 3.3.1.7.5.7 During the test run, make periodic adjustments to keep the temperature around the filter holder (and cyclone, if used) at the proper level. Add more ice, and, if necessary, salt to maintain a temperature of <20°C (68°F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.
- 3.3.1.7.5.8 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, it may be replaced in the midst of a sample run. Using another complete filter holder assembly is recommended, rather than attempting to change the filter itself. After a new filter assembly is installed, conduct a leak-check. If determined, the total particulate weight shall include the summation of all filter assembly catches.
- 3.3.1.7.5.9 If the condensate impinger becomes too full, it may be emptied, recharged with 50 ml of  $0.1\ N\ H_2SO_4$ , and replaced during the sample run. The condensate emptied must be saved and included in the measurement of the volume of moisture collected and included in the sample for analysis. The additional 50 ml of absorbing reagent must also be considered in calculating the moisture. After the impinger is reinstalled in the train, conduct a leak-check.
- 3.3.1.7.5.10 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

- 3.3.1.7.5.11 Note that when two or more trains are used, separate analyses of the particulate catch (if applicable) and the HCl and  $\mathrm{Cl}_2$  impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains. In that case, the particulate catch and the HCl and  $\mathrm{Cl}_2$  impinger catches from the individual trains may be combined, and a single particulate analysis and single HCl and  $\mathrm{Cl}_2$  analyses of the impinger contents may be performed.
- 3.3.1.7.5.12 At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, and record the final dry gas meter reading.
- 3.3.1.7.5.13 If there is any possibility that liquid has collected in the glass cyclone and/or on the filter, connect the Ascarite tube at the probe inlet and operate the train with the filter heating system at  $120 \pm 14^{\circ}\text{C}$  (248  $\pm$  25°F) at a low flow rate (e.g.,  $\Delta H = 1$ ) sufficient to vaporize the liquid and any HCl in the cyclone or on the filter and pull it through the train into the impingers. After 30 minutes, turn off the flow, remove the Ascarite tube, and examine the cyclone and filter for any visible moisture. If moisture is visible, repeat this step for 15 minutes.
- 3.3.1.7.5.14 Conduct a post-test leak check. Also, leak-check the pitot lines as described in EPA Method 2. The lines must pass this leak-check in order to validate the velocity-head data.
- 3.3.1.7.5.15 If the moisture value is available, calculate percent isokineticity (see Section 3.3.1.7.7.10) to determine whether the run was valid or another test run should be conducted.

### 3.3.1.7.6 Sample Recovery.

3.3.1.7.6.1 Allow the probe to cool. When the probe can be handled safely, wipe off all the external surfaces of the tip of the probe nozzle and place a cap over the tip. Do not cap the probe tip tightly while the sampling

train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the holder.

- 3.3.1.7.6.2 Before moving the sampling train to the cleanup site, remove the probe, wipe off any silicone grease, and cap the open outlet, being careful not to lose any condensate that might be present. Wipe off any silicone grease and cap the filter or cyclone inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger and the filter holder, disconnect it at the filter holder and let any condensed water drain into the first impinger. Wipe off any silicone grease and cap the filter holder outlet and the impinger inlet. Ground glass stoppers, plastic caps, serum caps, Teflon tape, Parafilm<sup>R</sup>, or aluminum foil may be used to close these openings.
- 3.3.1.7.6.3 Transfer the probe and filter/impinger assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.
- 3.3.1.7.6.4 Save portions of all washing solutions used for cleanup (acetone and Type II water) and the absorbing reagents (0.1 N  $\rm H_2SO_4$  and 0.1 N NaOH) as blanks. Transfer 200 ml of each solution directly from the wash bottle being used (rinse solutions) or the supply container (absorbing reagents) and place each in a separate, prelabeled glass sample container.
- 3.3.1.7.6.5 Inspect the train prior to and during disassembly and note any abnormal conditions.
- 3.3.1.7.6.6 Container No. 1 (filter catch for particulate determination). Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Use one or more pair of tweezers to handle the filter. If it is necessary to fold the filter, ensure that the particulate cake is inside the fold. Carefully transfer to the Petri dish any particulate matter or filter fibers that adhere to the filter holder gasket, using a dry nylon bristle brush or sharp-edged blade, or both. Label the container and seal with Teflon tape around the circumference of the lid.

- 3.3.1.7.6.7 Container No. 2 (front-half rinse for particulate determination). Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone into a glass container. Retain an acetone blank and analyze with the samples.
- 3.3.1.7.6.8 Perform rinses as follows: carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particles; then make a final rinse of the inside surface with the acetone. Brush and rinse the inside parts of the Swagelok fitting with the acetone in a similar way until no visible particles remain.
- 3.3.1.7.6.9 Have two people rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with solvent. Let the acetone drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washed to the container.
- 3.3.1.7.6.10 Follow the acetone rinse with a probe brush. Hold the probe in an inclined position and squirt acetone into the upper end while pushing the probe brush through the probe with a twisting action; place a sample container underneath the lower end of the probe and catch any acetone and particulate matter that is brushed from the probe. Run the brush through the probe three or more times until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above. Between sampling runs, keep brushes clean and protected from contamination.
- 3.3.1.7.6.11 Clean the inside of the front half of the filter holder and cyclone by rubbing the surfaces with a nylon bristle brush and

rinsing with acetone. Rinse each surface three times, or more if needed, to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if applicable). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all rinses and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents.

- 3.3.1.7.6.12 Container No. 3 (knockout and acid impinger catch for moisture and HCl determination). Disconnect the impingers. Measure the liquid in the acid and knockout impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these impingers, connecting glassware (and tubing, if used), and the back half of the filter holder with water and add these rinses to the storage container. Seal the container, shake to mix, and label. The fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Retain rinse water and acidic absorbing solution blanks and analyze with the samples.
- 3.3.1.7.6.13 Container No. 4 (alkaline impinger catch for Cl<sub>2</sub> and moisture determination). Measure and record the liquid in the alkaline impingers as described in Section 3.3.1.7.6.12. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container. Seal the container, shake to mix, and label; mark the fluid level. Retain alkaline absorbing solution blank and analyze with the samples.
- 3.3.1.7.6.14 Container No. 5 (silica gel for moisture determination). Note the color of the indicating silica gel to determine if it has

been completely spent and make a notation of its condition. Transfer the silica gel from the last impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere strongly to the impinger wall. Because the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the container and its contents to 0.5 g or better.

- 3.3.1.7.6.15 Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright and all particulate filters with the particulate catch facing upward.
- 3.3.1.7.7 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

#### 3.3.1.7.7.1 Nomenclature.

- $A_n$  = Cross-sectional area of nozzle,  $m^2$  (ft<sup>2</sup>).
- $B_{\omega x}$  = Water vapor in the gas stream, proportion by volume.
- C. = Acetone blank residue concentration, mg/mg.
- C<sub>d</sub> = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.
- c<sub>s</sub> = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
- I = Percent of isokinetic sampling.
- $m_a$  Mass of residue of acetone after evaporation, mg.
- $M_{\rm p}$  = Total amount of particulate matter collected, mg.
- $M_d$  = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).

- $M_w$  = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
- $P_{bar}$  Barometric pressure at the sampling site, mm Hg (in. Hg).
- P<sub>s</sub> Absolute stack-gas pressure, mm Hg (in. Hg).
- P<sub>std</sub> Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
- R = Ideal gas constant,  $0.06236 \text{ mm Hg-m}^3$  (K-g-mole (21.85 in. Hg-ft<sup>3</sup>/°R-lb-mole).
- $T_m$  = Absolute average dry-gas meter temperature (see Figure 2),  ${}^{\circ}K$  ( ${}^{\circ}R$ ).
- T<sub>s</sub> = Absolute average stack-gas temperature (see Figure 2), °K (°R).
- $T_{std}$  = Standard absolute temperature, 293°K (528°R).
- $V_{1c}$  Total volume of liquid collected in the impingers and silica gel, ml.
- $V_m$  = Volume of gas sample is measured by dry-gas meter, dscm (dscf).
- $V_{m(std)}$  Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).
- $V_{w(std)}$  = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
  - $V_s$  = Stack-gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).
  - Wa Weight of residue in acetone wash, mg.
  - V. Volume of acetone blank, ml.
  - V<sub>aw</sub> Volume of acetone used in wash; ml.
  - Y Dry-gas-meter calibration factor, dimensionless.
  - $\Delta H$  Average pressure differential across the orifice meter, mm  $H_2O$  (in  $H_2O$ ).
  - $\rho_a$  = Density of acetone, mg/ $\mu$ l (see label on bottle).
  - $\rho_{w}$  = Density of water, 0.9982 g/ml (0.002201 lb/ml).
  - $\theta$  = Total sampling time, min.

13.6 - Specific gravity of mercury.

60 = Sec/min.

100 - Conversion to percent.

- 3.3.1.7.7.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 3.3-2).
- 3.3.1.7.7.3 Dry gas volume. Correct the sample measured by the dry gas meter to standard conditions (20°C, 760 mm Hg [68°F, 29.92 in. Hg]) by using Equation 1:

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar} + \Delta H/13.6}{P_{std}} = K_1 V_m Y \frac{P_{bar} + \Delta H/13.6}{T_m}$$
 (1)

where:

 $K_1 = 0.3858$  K/mm Hg for metric units, or  $K_1 = 17.64^{\circ}$ R/in. Hg for English units.

3.3.1.7.7.4 Volume of water vapor.

$$V_{w(std)} = V_{1c} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{1c}$$
 (2)

where:

 $K_2$  = 0.001333 m³/ml for metric units, or  $K_2$  = 0.04707 m³/ml for English units.

3.3.1.7.7.5 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}$$
(3)

NOTE: In saturated or water-droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 3) and a second from the assumption of saturated conditions. The lower of the two values of  $B_w$  shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note to Section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is  $\pm 1^{\circ}C$  ( $2^{\circ}F$ ).

3.3.1.7.7.6 Acetone blank concentration. For particulate determination.

$$C_{\mathbf{a}} = \frac{\mathbf{m}_{\mathbf{a}}}{\mathbf{V}_{\mathbf{a}}\rho_{\mathbf{a}}} \tag{4}$$

3.3.1.7.7.7 Acetone wash blank. For particulate determination.

$$W_a = C_a V_{aw} \Delta_a \tag{5}$$

3.3.1.7.7.8 Total particulate weight. Determine the total particulate catch from the sum of the weights obtained from Container Nos. 1 and 2 less the acetone blank  $(W_a)$ .

3.3.1.7.7.9 Particulate concentration.

$$c_s = (0.001 \text{ g/mg})(m_n/V_{m(std)})$$
 (6)

3.3.1.7.7.10 Isokinetic variation.

3.3.1.7.7.4.10.1 Calculation from raw data.

$$I = \frac{100 T_s [K_3 F_{1c} + (V_m/T_m) (P_{bar} + H/13.6)]}{60 \theta V_s P_s A_n}$$
(7)

where:

 $K_3$  = 0.003454 mm Hg-m³/ml-K for metric units, or  $K_3$  = 0.002669 in. Hg-ft³/ml °R for English units.

3.3.1.7.4.10.2 Calculation for intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} V_s \theta A_n P_s 60 (1-B_{ws})}$$
(8)

$$= K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \theta (1-B_{ws})}$$
(8)

where:

 $K_4 = 4.320$  for metric units, or  $K_4 = 0.09450$  for English units.

3.3.1.7.4.10.3 Acceptable units. If 90 percent  $\leq I \leq 110$  percent, the results are acceptable. If the results are low in comparison with the standard and I is beyond the acceptable range, or if I is less than 90 percent, the Administrator may opt to accept the results.

## 3.3.1.8 Quality Control

- 3.3.1.8.1 Sampling. See EPA Manual 600/4-77-027b for Method 5 quality control.
- 3.3.1.8.2 Analysis. At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

#### 3.3.1.9 Method Performance

- 3.3.1.9.1 The in-stack detection limit for the method is approximately 0.02  $\mu g$  of HCl per liter of stack gas. The method has a negative bias below 20 ppm HCl (Reference 6).
- 3.3.1.9.2 It is preferable to include the cyclone in the sampling train to protect the filter from any moisture present. There is research in progress regarding the necessity of the cyclone at low moisture sources and the use of Ascarite II in the drying procedure (Section 3.3.1.7.5.12).

#### REFERENCES

- 1. U.S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Methods 1-5.
- 2. U.S. Environmental Protection Agency, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods," Publication No. EPA-600/4-77-027b, August 1977.
- 3. Shigehara, R.T., Adjustments in the EPA Nomography for Different Pitot Tube Coefficients and Dry Molecular Weights, Stack Sampling News,  $\underline{2}$ :4-11 (October 1974).
- 4. Steinsberger, S.C. and J.H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. EPA 600/3-89/064, NTIS PB89 220586-AS.
- 5. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid emissions from Stationary Sources," March 18, 1987.
- 6. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report," EPA Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.

## 3.3.2 <u>Midget Impinger HCl/Cl<sub>2</sub> Emission Sampling Train (Method 0051)</u>

## 3.3.2.1 Scope and Application

3.3.2.1.1 This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl<sub>2</sub>, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators, municipal waste combustors, and boilers and industrial furnaces. The collected samples are analyzed using Method 9057. This method is designed to collect  $HCl/Cl_2$  in their gaseous forms. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter (e.g., HCl dissolved in water droplets) must be sampled using an isokinetic  $HCl/Cl_2$  sampling train (see Method 0050).

### 3.3.2.2 Summary of Method

3.3.2.2.1 An integrated gas sample is extracted from the stack and passes through a particulate filter, acidified water, and finally through an alkaline solution. The filter serves to remove particulate matter such as chloride salts which could potentially react and form analyte in the absorbing solutions. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions (Cl<sup>-</sup>) as follows:

$$HC1 + H_2O = H_3O^+ + C1^-$$

The  $Cl_2$  gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton  $(H^+)$ ,  $Cl^-$ , and hypochlorous acid (HClO) as follows:

$$H_2O + Cl_2 = H^+ + Cl^- + HClO$$

The Cl<sup>-</sup> ions in the separate solutions are measured by ion chromatography (Method 9057).

#### 3.3.2.3 Interferences

- 3.3.2.3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine ( $\mathrm{Cl_2}$ ) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water.  $\mathrm{Cl_2}$  gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm  $\mathrm{Cl_2}$  with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm  $\mathrm{Cl_2}$  results in a positive bias of 3.4 percent in the HCl measurement.
- 3.3.2.3.2 Reducing agents such as  ${\rm SO}_2$  may cause a positive bias in the  ${\rm Cl}_2$  measurement by the following reaction:

$$HC10 + HSO_3^- = H_2SO_4 + C1^-$$

### 3.3.2.4 Apparatus and Materials

- 3.3.2.4.1 Sampling Train. The sampling train is shown in Figure 1 and component parts are discussed below.
- 3.3.2.4.1.1 Probe. Borosilicate glass, approximately 3/8-in (9-mm) inside diameter, with a heating system to prevent condensation. When the concentration of alkaline particulate matter in the emissions is high, a 3/8-in (9-mm) inside diameter Teflon elbow should be attached to the inlet of the probe; a 1-in (25-mm) length of Teflon tubing with a 3/8-in (9-mm) inside diameter should be attached at the open end of the elbow to permit the opening of the probe to be burned away from the gas stream, thus reducing the amount of particulate entering the train. When high concentrations of particulate matter are not present, the Teflon elbow is not necessary, and the probe inlet can be perpendicular to the gas stream. When sampling at locations where gas temperatures are greater than approximately 400°F, such as wet scrubber inlets, glass or quartz elbows must be used. In no case should a glass wool

plug be used to remove particulate matter; use of such a filtering device could result in a bias in the data. Instead, a Teflon filter should be used as specified in Section 3.3.2.5.5.

- 3.3.2.4.1.2 Three-way stopcock. A borosilicate, three-way glass stopcock with a heating system to prevent condensation. The heated stopcock should connect directly to the outlet of the probe and filter assembly and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.
- 3.3.2.4.1.3 Impingers. Five 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for extended sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.
- 3.3.2.4.1.4 Mae West impinger or drying tube. Mae West design impinger (or drying tube, if a moisture determination is not to be conducted) filled with silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump.
- 3.3.2.4.1.5 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.
- 3.3.2.4.1.6 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for the elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

- 3.3.2.4.1.7 Purge pump, purge line, drying tube, needle valve, and rate meter. Pump capable of purging sample probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter, 0 to 5 liters/min.
- 3.3.2.4.1.8 Metering system. The following items comprise the metering system which is identical to that used for EPA Method 6 (see Reference 5).
- 3.3.2.4.1.8.1 Valve. Needle valve, to regulate sample gas flow rate.
- 3.3.2.4.1.8.2 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through train. Install a small surge tank between the pump and the rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.
- 3.3.2.4.1.8.3 Rate meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of selected flow rate of 2 liters/min.
- 3.3.2.4.1.8.4 Volume meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions encountered during sampling, and equipped with a temperature gauge (dial thermometer or equivalent) capable of measuring temperature to within  $3^{\circ}$ C (5.4°F).
- 3.3.2.4.1.8.5 Vacuum gauge. At least 760 mm Hg (30 in. Hg) gauge to be used for leak check of the sampling train.
  - 3.3.2.4.2 Sample Recovery.
- 3.3.2.4.2.1 Wash bottles. Polyethylene or glass, 500 ml or larger, two.

3.3.2.4.2.2 Storage bottles. Glass, with Teflon-lined lids, 100 ml, to store impinger samples (two per sampling run).

### 3.3.2.5 Reagents

- 3.3.2.5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 3.3.2.5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. It is advisable to analyze a blank sample of this reagent <u>prior</u> to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see Method 9057).
- 3.3.2.5.3 Sulfuric acid (0.1 N),  $H_2SO_4$ . Used as the HCl absorbing reagent. To prepare 100 ml, slowly add 0.28 ml of concentrated  $H_2SO_4$  to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see Method 9057).
- 3.3.2.5.4 Sodium hydroxide (0.1 N), NaOH. Used as the  $\mathrm{Cl_2}$  absorbing reagent. To prepare 100 ml, dissolve 0.40 g of solid NaOH in about 90 ml of water and adjust the final volume to 100 ml using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see Method 9057).

- 3.3.2.5.5 Filter. Teflon mat Pallflex<sup>R</sup> TX40HI75 or equivalent. Locate in a glass, quartz, or Teflon filter holder with a Teflon filter support in a filter box heated to 250°F.
- 3.3.2.5.6 Stopcock grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.
- 3.3.2.5.7 Silica gel. Indicating type, 6- to 16-mesh. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.
  - 3.3.2.6 Sample Collection, Preservation, and Handling
- 3.3.2.6.1 Sample collection is described in this method. The analytical procedures are described in Method 9057.
- 3.3.2.6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

#### 3.3.2.7 Procedure

- 3.3.2.7.1 Calibration. Section 3.5.2 of EPA's Quality Assurance Handbook, Volume III (Reference 4) may be used as a guide for these operations.
  - 3.3.2.7.1.1 Dry Gas Metering System.
- 3.3.2.7.1.1.1 Initial calibration. Before its initial use in the field, first leak check the metering system (sample line, drying tube, if used, vacuum gauge, needle valve, pump, rate meter, and dry gas meter) as follows: plug the inlet end of the sampling line, pull a vacuum of 250 mm (10 in) Hg, plug off the outlet of the dry gas meter, and turn off the pump. The vacuum should remain stable for 30 seconds. Carefully release the vacuum from

the system by slowly removing the plug from the sample line inlet. Remove the sampling line (and drying tube, if applicable), and connect the dry gas metering system to an appropriately sized wet test meter (e.g., 1 liter per revolution). Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, with both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

- 3.3.2.7.1.1.2 Post-test calibration check. After each field test series, conduct a calibration check as in Section 3.3.2.7.1.1.1 above, except for the following variations: (a) the leak check is not to be conducted, (b) three or more revolutions of the dry gas meter may be used, (c) only two independent runs need to be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in Section 3.3.2.7.1.1.1), the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as Section 3.3.2.7.1.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.
- 3.3.2.7.1.2 Thermometer(s). Prior to each field test, calibrate against mercury-in-glass thermometers at ambient temperature. If the thermometer being calibrated reads within 2°C (2.6°F) of the mercury-in-glass thermometer, it is acceptable. If not, adjust the thermometer or use an appropriate correction factor.
- 3.3.2.7.1.3 Rate meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.
- 3.3.2.7.1.4 Barometer. Prior to each field test, calibrate against a mercury barometer. The field barometer should agree within 0.1 in. Hg with

the mercury barometer. If it does not, the field barometer should be adjusted.

### 3.3.2.7.2 Sampling.

- 3.3.2.7.2.1 Preparation of collection train. Prepare the sampling train as follows: The first or knockout impinger should have a shortened stem and be left empty to condense moisture in the gas stream. The next two midget impingers should each be filled with 15 ml of  $0.1\ N\ H_2SO_4$ , and the fourth and fifth impingers should each be filled with 15 ml of  $0.1\ N\ NaOH$ . Place a fresh charge of silica gel, or equivalent, in the Mae West impinger (or the drying tube). Connect the impingers in series with the knockout impinger first, followed by the two impingers containing the acidified reagent, the two impingers containing the alkaline reagent, and the Mae West impinger containing the silica gel. If the moisture will be determined, weigh the impinger assembly to the nearest  $\pm\ 0.5\ g$  and record the weight.
- 3.3.2.7.2.2 Leak check procedures. Leak check the probe and threeway stopcock prior to inserting the probe into the stack. Connect the stopcock to the outlet of the probe, and connect the sample line to the needle valve. Plug the probe inlet, turn on the sample pump, and pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Place the probe in the stack at the sampling location, and adjust the filter heating system to 250°F and the probe and stopcock heating systems to a temperature sufficient to prevent water condensation. Connect the first impinger to the stopcock, and connect the sample line to the last impinger and the needle valve. Upon completion of a sampling run, remove the probe from the stack and leak check as described above. If a leak has occurred, the sampling run must be voided. Alternatively, the portion of the train behind the probe may be leak checked between multiple runs at the same site as follows: Close the stopcock to the first impinger (see Figure 3.3-3A), and turn on the sample pump. Pull a vacuum of at least 250 mm Hg (10 in. Hg), turn off the needle valve, and note the vacuum gauge reading.

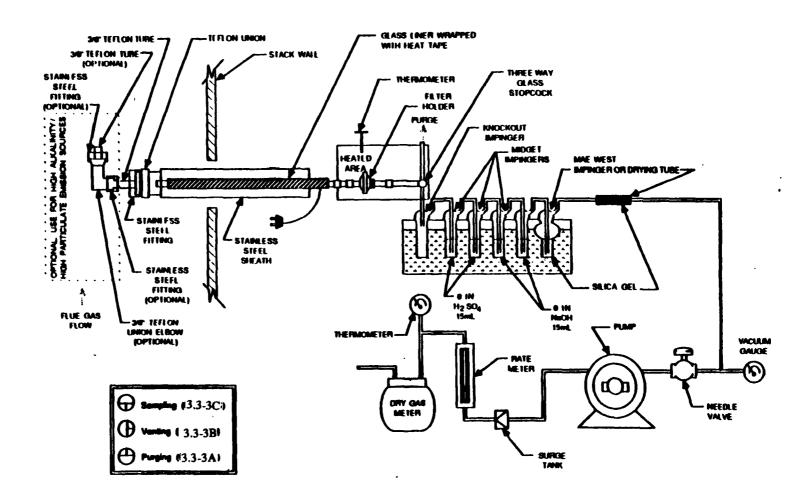


Figure 3.3-3 Midget Impinger  $\mathrm{HC1/Cl}_2$  Sampling Train

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should remain stable for at least 30 seconds. Release the vacuum on the impinger train by turning the stopcock to the vent position to permit ambient air to enter (see Figure 3.3-3B). If this procedure is used, the full train leak check described above must be conducted following the final run and all preceding sampling runs voided if a leak has occurred.

- 3.3.2.7.2.3 Purge procedure. Immediately prior to sampling, connect the purge line to the stopcock and turn the stopcock to permit the purge pump to purge the probe (see Figure 3.3-3A). Turn on the purge pump, and adjust the purge rate to 2 liters/min. Purge for at least 5 minutes prior to sampling.
- 3.3.2.7.2.4 Sample collection. Turn on sample pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 3.3-3C). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate within 10 percent during the entire sampling run. Take readings of the dry gas meter, the dry gas meter temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. However, if the expected condensate catch for this sampling run duration will exceed the capacity of the sampling train, (1) a larger knockout impinger may be used or (2) two sequential half-hour runs may be conducted. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak check as described in Section 3.3.2.7.2.2.
- 3.3.2.7.3 Sample recovery. Following sampling, disconnect the impinger train from the remaining sampling equipment at the inlet to the knockout impinger and the outlet to the last impinger. If performing a moisture determination, wipe off any moisture on the outside of the train and any excess silicone grease at the inlet and outlet openings; weigh the train to the nearest 0.5 g and record this weight. Then disconnect the impingers from each other. Quantitatively transfer the contents of the first three impingers (the knockout impinger and the two 0.1 N H<sub>2</sub>SO<sub>4</sub> impingers) to a leak-free storage bottle. Add the water rinses of each of these impingers and

connecting glassware from the second set of impingers (containing the 0.1 N NaOH) should be recovered in a similar manner if a  $\rm Cl_2$  analysis is desired. The sample bottle should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Save portions of the 0.1 N  $\rm H_2SO_4$  and 0.1 N NaOH used as impinger reagents as reagent blanks. Take 50 ml of each and place in separate leak-free storage bottles. Label and mark the fluid levels as previously described.

3.3.2.7.4 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

#### 3.3.2.7.4.1 Nomenclature.

 $B_{ws}$  - Water vapor in the gas stream, proportion by volume.

 $M_w$  = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

 $P_{bar}$  = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).

 $P_{\text{std}}$  = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant,  $0.06236 \text{ mm Hg-m}^3/^\circ \text{K-g-mole}$  (21.85 in. Hg-ft<sup>3</sup>/ $^\circ \text{R-lb-mole}$ ).

 $T_m$  = Average dry gas meter absolute temperature, °K (°R).

 $T_{\text{std}}$  - Standard absolute temperature, 293°K (528°R).

V<sub>1c</sub> = Total volume of liquid collected in impingers and silica gel, ml (equivalent to the difference in weight of the impinger train before and after sampling, 1 mg = 1 ml).

V<sub>m</sub> - Dry gas volume as measured by the dry gas meter, dcm (dcf).

 $V_{m(std)}$  - Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

 $V_{w(std)}$  - Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

Y - Dry gas meter calibration factor.

 $\rho_{\rm w}$  = Density of water, 0.9982 g/ml (0.002201 lb/ml).

3.3.2.7.4.2 Sample volume, dry basis, corrected to standard conditions. Calculate as described below:

$$V_{m(std)} - V_{m}Y \left[\begin{array}{c} T_{std} \\ \hline T_{m} \end{array}\right] \left[\begin{array}{c} P_{bar} \\ \hline P_{std} \end{array}\right] - K_{1} Y \frac{V_{m} P_{bar}}{T_{m}}$$
 (1)

where:

 $K_1 = 0.3858^{\circ}K/mm$  Hg for metric units. = 17.64°R/in. Hg for English units.

3.3.2.7.4.3 Volume of water vapor.

$$V_{w(std)} = V_{1c} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{1c}$$
 (2)

where:

 $K_2$  = 0.0013333 m<sup>3</sup>/ml for metric units. = 0.04707 ft<sup>3</sup>/ml for English units.

3.3.2.7.4.4 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}$$
(3)

#### 3.3.2.8 Quality Control

3.3.2.8.1 At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

#### 3.3.2.9 Method Performance

- 3.3.2.9.1 The in-stack detection limit for the method is approximately 0.08  $\mu g$  of HCl per liter of stack gas for a 1-hour sample.
- 3.3.2.9.2 The precision and bias for measurement of HCl using this sampling protocol combined with the analytical protocol of Method 9057 have been determined. The within laboratory relative standard deviation is 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at  $\text{Cl}_2$  concentrations less than 50 ppm.

#### REFERENCES

- Steinsberger, S.C. and J.H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. EPA 600/3-89/064, NTIS PB 89 220586-AS.
- 2. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources," March 18, 1987.
- 3. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report," EPA Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.
- 4. U.S. Environmental Protection Agency, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods," Publication No. EPA-600/4-77-027b, August 1977.
- U.S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Method 6.

# 3.3.3 <u>Protocol for Analysis of Samples from HCl/Cl<sub>2</sub> Emission Sampling Train (Method 9057)</u>

#### 3.3.3.1 Scope and Application

- 3.3.3.1.1 This method describes the analytical protocol for determination of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chloride (Cl<sub>2</sub>, CAS Registry Number 7782-50-5) in stack gas emission samples collected from hazardous waste and municipal waste incinerators using the midget impinger HCl/Cl<sub>2</sub> sampling train (Method 0051) or the isokinetic HCl/Cl<sub>2</sub> sampling train (Method 0050).
- 3.3.3.1.2 The lower detection limit is  $0.1~\mu g$  of chloride (Cl<sup>-</sup>) per ml of sample solution. Samples with concentrations which exceed the linear range of the analytical instrumentation may be diluted.
- 3.3.3.1.3 This method is recommended for use only by analysts experienced in the use of ion chromatography and in the interpretation of ion chromatograms.

#### 3.3.3.2 Summary of Method

3.3.3.2.1 The stoichiometry of HCl and  $\text{Cl}_2$  collection in the sampling train (see Methods 0050 and 0051) is as follows: In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions (Cl<sup>-</sup>) according to the following formula:

$$HC1 + H_2O - H_3O^+ + C1^-$$

The  $Cl_2$  gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton  $(H^+)$ ,  $Cl^-$ , and hypochlorous acid (HClO) as shown:

$$H_2O + Cl_2 = H^+ + Cl^- + HClO$$

Non-suppressed or suppressed ion chromatography (IC) is used for analysis of the  ${\rm Cl}^-$ .

#### 3.3.3.3 Interferences

- 3.3.3.3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One likely interferant is diatomic chlorine ( $\mathrm{Cl}_2$ ) gas which disproportionates to HCl and hypochlorous acid (HOCl) upon dissolution in water.  $\mathrm{Cl}_2$  gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm  $\mathrm{Cl}_2$  with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm  $\mathrm{Cl}_2$  results in a positive bias of 3.4 percent in the HCl measurement. Other interferants have not been encountered.
- 3.3.3.2 Reducing agents such as  ${\rm SO}_2$  may cause a positive bias in the  ${\rm Cl}_2$  measurement by the following reaction:

$$HC10 + HSO_3^- = H_2SO_4 + C1^-$$

- 3.3.3.4 Apparatus and Materials
- 3.3.3.4.1 Volumetric Flasks. Class A, various sizes.
- 3.3.3.4.2 Volumetric Pipettes. Class A, assortment, to dilute samples to calibration range of the IC.
- 3.3.3.4.3 Ion Chromatograph. Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, a strip chart recorder, and peak heights may be used provided the 5 percent repeatability criteria for sample analysis and the linearity criteria for the calibration curve can be met.

#### 3.3.3.5 Reagents

- 3.3.3.5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 3.3.3.5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.
- 3.3.3.5.3 Sulfuric acid (0.1 N),  $H_2SO_4$ . To prepare 100 ml, slowly add 0.28 ml of concentrated  $H_2SO_4$  to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.
- 3.3.3.5.4 Sodium hydroxide (0.1 N), NaOH. To prepare 100 ml, dissolve 0.40 g of solid NaOH in about 90 ml of water and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.
- 3.3.3.5.5 Reagent blank solutions. A separate blank solution of each sampling train reagent used and collected in the field (0.1 N  $\rm H_2SO_4$  and 0.1 N NaOH) should be prepared for analysis with the field samples. For midget impinger train sample analysis, dilute 30 ml of each reagent with rinse water collected in the field as a blank to the final volume of the samples; for isokinetic train sample analysis, dilute 200 ml to the same final volume as the field samples also using the blank sample of rinse water.
- 3.3.3.5.6 Sodium chloride, NaCl, stock standard solution. Solutions containing a nominal certified concentration of 1000 mg/L NaCl are commercially available as convenient stock solutions from which working standards can be made by appropriate volumetric dilution. Alternately, concentrated stock solutions may be produced from reagent grade NaCl that has

been dried at 110°C for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. The exact Cl<sup>-</sup> concentration can be calculated using the equation:

 $\mu$ g Cl<sup>-</sup>/ml = g of NaCl x 10<sup>3</sup> x 35.453/58.44

Refrigerate the stock standard solutions and store no longer than one month.

- 3.3.3.5.7 Chromatographic eluent. Effective eluents for non-suppressed ion chromatography using a resin- or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to a pH of 4.0 using a saturated sodium borate solution, and a mM 4-hydroxy benzoate solution, adjusted to a pH of 8.6 using 1 N sodium hydroxide. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH that contain no ions interfering with the chromatographic analysis may be used. If, using suppressed ion chromatography, the "water dip" resulting from sample injection is interfering with the chlorine peak, use a 2 mM sodium hydroxide/2.4 mM sodium bicarbonate eluent.
  - 3.3.3.6 Sample Collection, Preservation, and Handling
- 3.3.3.6.1 Sample collection using the midget impinger HCl/Cl<sub>2</sub> train or the isokinetic HCl/Cl<sub>2</sub> train is described in Method 0051 or 0050, respectively.
- 3.3.3.6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

#### 3.3.3.7 Procedure

3.3.3.7.1 Sample preparation for analysis. Check the liquid level in each sample, and determine if any sample was lost during shipment. If a

noticeable amount of leakage has occurred, the volume can be determined from the difference between the initial and final solution levels, and this value can be used to correct the analytical results. For midget impinger train samples, quantitatively transfer each sample solution to a 100 ml volumetric flask and dilute to 100 ml with water. For isokinetic sampling train samples, quantitatively transfer each sample to a volumetric flask or graduated cylinder and dilute with water to a final volume appropriate for all samples.

#### 3.3.3.7.2 Calibration of Ion Chromatograph.

- 3.3.3.7.2.1 The ion chromatographic conditions will depend on the type of analytical column used and whether suppressed or non-suppressed ion chromatography is used. Prior to calibration and sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl appears in the chromatogram. If Cl is present, repeat the load/injection procedure until no Cl is present.
- 3.3.3.7.2.2 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solution to convenient volumes, using  $0.1~{\rm H_2SO_4}$  or  $0.1~{\rm NaOH}$  as appropriate. Prepare at least four standards that are within the linear range of the field samples. Inject the calibration standards, starting with the lowest concentration standard first, both before and after injection of the quality control check sample, reagent blank, and field samples. This allows compensation for any instrument drift occurring during sample analysis.
- 3.3.3.7.2.3 Determine the peak areas, or heights, of the standards and plot individual values versus Cl concentrations in  $\mu g/ml$ . Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.
- 3.3.3.7.3 Sample analysis. Between injections of the series of calibration standards, inject in duplicate the reagent blanks and the field samples, including a matrix spike sample. Measure the areas or heights (same as done for the calibration standards) of the Cl peaks. Use the average

response to determine the concentrations of the field samples, matrix spike, and reagent blanks using the linear calibration curve. The results for a reagent blank should not exceed 10 percent of the corresponding value for a field sample.

3.3.3.7.4 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

3.3.3.7.4.1 Total  $\mu g$  HCl per sample. Calculate as described below:

$$^{\text{m}}HC1 = (S-B) \times V_{\text{s}} \times 36.46/35.453$$
 (1)

where:  ${}^{m}HCl = Mass of HCl in sample, \mu g$ ,

S = Analysis of sample,  $\mu$ g Cl<sup>-</sup>/ml,

B = Analysis of reagent blank,  $\mu$ g Cl<sup>-</sup>/ml,

 $V_{x}$  - Volume of filtered and diluted sample, ml,

36.46 = Molecular weight of HCl,  $\mu g/\mu g$ -mole, and

35.45 = Atomic weight of Cl<sup>-</sup>,  $\mu g/\mu g$ -mole.

3.3.3.7.4.2 Total  $\mu$ g Cl<sub>2</sub> per sample. Calculate as described below:

$$^{M}Cl_{2} = (S-B) \times V_{2} \times 70.91/35.45$$
 (2)

where:  ${}^{M}Cl_{2}$  - Mass of  $Cl_{2}$  in sample,  $\mu g$ ,

70.91 = Molecular weight of  $Cl_2$ ,  $\mu g/\mu g$ -mole, and

35.45 - Atomic weight of Cl<sup>-</sup>,  $\mu g/\mu g$ -mole.

3.3.3.7.4.3 Concentration of HCl in the flue gas. Calculate as described below:

$$C = K \times m/V_{m(std)}$$
 (3)

where: C = Concentration of HCl or Cl<sub>2</sub>, dry basis, mg/dscm,

 $K = 10^{-3} \text{ mg/}\mu\text{g}$ 

= Mass of HCl or  $Cl_2$  in sample,  $\mu g$ , and

 $V_{m(std)}$  = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (from Method 0050 or Method 0051).

#### 3.3.3.8 Quality Control

- 3.3.3.8.1 At the present time, a validated audit material does not exist for this method. However, it is strongly recommended that a quality control check sample and a matrix spike sample be used.
- 3.3.3.8.1.1 Quality control check sample. Chloride solutions of reliably known concentrations are available for purchase from the National Bureau of Standards (SRM 3182). The QC check sample should be prepared in the appropriate absorbing reagent at a concentration approximately equal to the mid range calibration standard. The quality control check sample should be injected in duplicate immediately after the calibration standards have been injected for the first time. The Cl value obtained for the check sample using the final calibration curve should be within 10 percent of the known value for the check sample.
- 3.3.3.8.1.2 Matrix spike sample. A portion of at least one field sample should be used to prepare a matrix spike sample. Spike the sample aliquot in the range of the expected concentration. Analyze the matrix spike sample in duplicate along with the field samples. Based on the matrix spike results, determine the recovery for the spiked material. This should be within 10 percent of the known spike value.

#### 3.3.3.9 Method Performance

- 3.3.3.9.1 The lower detection limit of the analytical method is 0.1  $\mu g$  of Cl per ml of sample solution. Samples with concentrations which exceed the linear range of the IC may be diluted.
- 3.3.3.9.2 The precision and bias for analysis of HCl using this analytical protocol have been measured in combination with the midget impinger  $HC1/Cl_2$  train (Method 0051) for sample collection. The within-laboratory relative standard deviation is 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at  $Cl_2$  concentrations less than 50 ppm.

#### REFERENCES

- Steinsberger, S.C. and J.H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. EPA 600/3-89/064, NTIS PB89 220586-AS.
- 2. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources," March 18, 1987.
- 3. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride emissions from Stationary Sources: Interim Report," EPA-Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.

3.4 <u>Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) from Stationary Sources (Method 23)</u>

#### 3.4.1 Applicability and Principle

- 3.4.1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) from stationary sources.
- 3.4.1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDDs and PCDFs are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

#### 3.4.2 Apparatus

- 3.4.2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 3.4-1. Sealing greases may not be used in assembling the train. The train is identical to that described in Section 2.1 of Method 5 (40 CFR Part 60, Appendix A) with the following additions:
- 3.4.2.1.1 Reagents. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 3.4.2.1.2 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

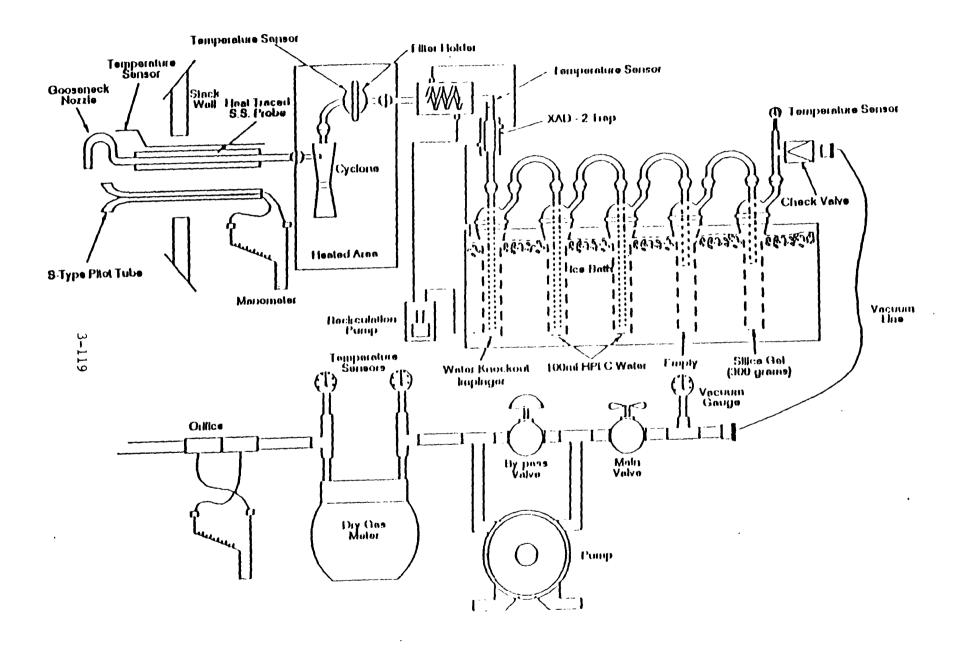


Figure 3.4-1 Sampling Train

- 3.4.2.1.3 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat-traced, heavy walled TFE (1/2 in. OD with 1/8 in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120°C.
  - 3.4.2.1.4 Filter Support. Teflon or Teflon-coated wire.
- 3.4.2.1.5 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 3.4-2.
- 3.4.2.1.6 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at  $\leq 20^{\circ}\text{C}$  (68°F).
- 3.4.2.1.7 Adsorbent Module. Glass container to hold the solid adsorbent. A schematic diagram is shown in Figure 3.4-2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

Figure 3.4-2 Condenser and adsorbent trap

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- 3.4.2.2 Sample Recovery.
- 3.4.2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 3.4.2.2.6) to cap off the sample-exposed sections of the train.
  - 3.4.2.2.2 Wash Bottles. Teflon, 500-ml.
- 3.4.2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes.

  Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.
- 3.4.2.2.4 Filter Storage Container. Sealed filter holder, widemouth amber glass jar with Teflon-lined cap, or glass petri dish.
  - 3.4.2.2.5 Balance. Triple beam.
  - 3.4.2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.
- 3.4.2.2.7 Metal Storage Container. Air-tight container to store silica gel.
  - 3.4.2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.
- 3.4.2.2.9 Glass sample Storage container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak-free Teflon-lined caps.
  - 3.4.2.3 Analysis.
- 3.4.2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.
  - 3.4.2.3.2 Test Tube. Glass.

- 3.4.2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 x 123 mm extraction thimbles.
- 3.4.2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.
- 3.4.2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.
  - 3.4.2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.
  - 3.4.2.3.7 Rotary Evaporator. Buchi/Brinkman RF-121 or equivalent.
- 3.4.2.3.8 Nitrogen Evaporator Concentrator. N-Evap Analytical Evaporator Model III or equivalent.
  - 3.4.2.3.9 Separatory Funnels. Glass, 2-liter.
- 3.4.2.3.10 Gas Chromatograph. Consisting of the following components:
- 3.4.2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature  $\pm 1^{\circ}$ C and performing programmed increases in temperature at rates of at least  $3^{\circ}$ C/min.
- 3.4.2.3.10.2 Temperature Gauge. To monitor column, oven, detector, and exhaust temperatures  $\pm 1^{\circ}C$ .
- 3.4.2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.
- 3.4.2.3.10.4 Capillary Columns. A fused silica column,  $60 \times 0.25$  mm inside diameter (ID), coated with DB-5 and a fused silica column,  $30 \text{ m} \times 0.25$  mm ID coated with DB-225. Other column systems may be used provided that the user is able to demonstrate, using calibration and performance checks,

that the column system is able to meet the specifications of Section 3.4.6.1.2.2.

- 3.4.2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of  $\pm 5$  ppm.
- 3.4.2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.
  - 3.4.2.3.13 Analytical Balance. To measure within 0.1 mg.

## 3.4.3 Reagents

- 3.4.3.1 Sampling.
- 3.4.3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986-71 (Reapproved 1978) (incorporated by reference see §60.17).
- 3.4.3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble, 1 g of silica gel, and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the toluene extract, and retain it for analysis. Remove the filters and dry them under a clean  $N_2$  stream. Store the filters in a glass petri dish sealed with Teflon tape.
- 3.4.3.1.2 Adsorbent Resin. Amberlite XAD-2 resin, thoroughly cleaned before initial use.

3.4.3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order:

Procedure

Salment

Solvenc	rrocedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Methylene Chloride (fresh)	Extract for 22 hours.
3.4.3.1.2.2 Drying.	

- 3.4.3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.
- 3.4.3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as to cause the particles to fracture.

- 3.4.3.1.2.3 Quality Control Check. The adsorbent must be checked for residual methylene chloride as well as PCDDs and PCDFs.
- 3.4.3.1.2.3.1 Extraction. Weigh a 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.
- 3.4.3.1.2.3.2 Analysis. Inject a  $2-\mu l$  sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft x 1/8 in. stainless steel containing 10 percent OV-101 on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 ml/min.

Detector: Flame ionization detector operated at a sensitivity of 4  $\times$  10<sup>-11</sup> A/mV.

Injection Port Temperature: 250°C.

Detector Temperature: 305°C.

Oven Temperature: 30°C for 4 min; programmed to rise at 40°C/min until it reaches 250°C; return to 30°C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injecting 2.5  $\mu$ l of methylene chloride into 100 ml of toluene. This corresponds to 100  $\mu$ g of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000  $\mu$ g/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.4.3.1.2.3.3 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is

purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

- 3.4.3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110°C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.
- 3.4.3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.
- 3.4.3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for two hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.
- 3.4.3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.
  - 3.4.3.2 Sample Recovery.
  - 3.4.3.2.1 Acetone. Pesticide quality.
  - 3.4.3.2.2 Methylene Chloride. Pesticide quality.
  - 3.4.3.2.3 Toluene. Pesticide quality.
  - 3.4.3.3 Analysis.
- 3.4.3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.
- 3.4.3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

- 3.4.3.3.3 Sulfuric Acid. Reagent grade:
- 3.4.3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.
  - 3.4.3.3.5 Hexane. Pesticide grade.
  - 3.4.3.3.6 Methylene Chloride. Pesticide grade.
  - 3.4.3.3.7 Benzene. Pesticide grade.
  - 3.4.3.3.8 Ethyl Acetate.
  - 3.4.3.3.9 Methanol. Pesticide grade.
  - 3.4.3.3.10 Toluene. Pesticide grade.
  - 3.4.3.3.11 Nonane. Pesticide grade.
  - 3.4.3.3.12 Cyclohexane. Pesticide grade.
- 3.4.3.3.13 Basic Alumina. Activity grade 1, 100-200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130°C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.
- 3.4.3.3.14 Silica Gel. Bio-Sil A, 100-200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180°C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50°C for 10 minutes, and then increase the temperature gradually to 180°C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.
  - 3.4.3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine

100 g of silica gel with 44 g of concentrated sulfuric acid in a screw-capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

- 3.4.3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw-capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.
- 3.4.3.3.17 Carbon/Celite. Combine 10.7 g of AX-21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.
  - 3.4.3.3.18 Nitrogen. Ultra high purity.
  - 3.4.3.3.19 Hydrogen. Ultra high purity.
- 3.4.3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labeled PCDDs and PCDFs at the concentrations shown in shown in Table 3.4-1 under the heading "Internal Standards" in 10 ml of nonane.
- 3.4.3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labeled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Surrogate Standards" in 10 ml of nonane.
- 3.4.3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the isotopically labeled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Recovery Standards" in 10 ml of nonane.

.... Table 3.4-1

# COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)	
Internal Standards		
13C <sub>12</sub> -2,3,7,8-TCDD 13C <sub>12</sub> -1,2,3,7,8-PeCCD 13C <sub>12</sub> -1,2,3,6,7,8-HxCDD 13C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD 13C <sub>12</sub> -2,3,7,8-TCDF 13C <sub>12</sub> -1,2,3,7,8-PeCDF 13C <sub>12</sub> -1,2,3,6,7,8-HxCDF 13C <sub>12</sub> -1,2,3,6,7,8-HpCDF	100 100 100 100 100 100 100	
Surrogate Standards		
<sup>37</sup> C1 <sub>4</sub> -2,3,7,8-TCDD <sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD <sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF <sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF <sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	100 100 100 100 100	
Recovery Standards		
<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD <sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDD	500 500	

#### 3.4.4 Procedure

- 3.4.4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, analysts should be trained and experienced with the analytical procedures.
  - 3.4.4.1.1 Preparation Prior to Analysis.
- 3.4.4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in Section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.
- 3.4.4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD-2. Follow the XAD-2 with glass wool and tightly cap both ends of the trap. Add 100  $\mu$ l of the surrogate standard solution (Section 3.4.3.3.21) to each trap.
- 3.4.4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD-0576.
- 3.4.4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air-tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sample holder just prior to sampling.
- 3.4.4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

- 3.4.4.1.2 Preliminary Determinations. Same as Section 4.1.2 of Method 5.
  - 3.4.4.1.3 Preparation of Collection Train.
- 3.4.4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin. NOTE: Do not use sealant grease in assembling the train.
- 3.4.4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.
- 3.4.4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.
  - 3.4.4.1.3.4 Assemble the train as shown in Figure 3.4-1.
- 3.4.4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD-2 adsorbent resin temperature never exceed 50°C because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20°C for efficient capture of the PCDDs and PCDFs.
  - 3.4.4.1.4 Leak-Check Procedure. Same as Method 5, Section 4.1.4.
  - 3.4.4.1.5 Sample Train Operation. Same as Method 5, Section 4.1.5.

3.4.4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

- 3.4.4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.
- 3.4.4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.
- 3.4.4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by brushing while rinsing three times each with acetone, and then by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

3.4.4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in Section 3.4.4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

3.4.4.2.5 Impinger Water. Measure the liquid in the first three impingers to with  $\pm 1$  ml by using a graduated cylinder or by weighing it to within  $\pm 0.5$  g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

3.4.4.2.6 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal.

#### 3.4.5 Analysis

All glassware shall be cleaned as described in Section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

### 3.4.5.1 Sample Extraction.

- 3.4.5.1.1 Extraction System. Place an extractable thimble (Section 3.4.2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.
- 3.4.5.1.2 Container No. 1 (Filter). Transfer the contents of container number 1 directly to the glass thimble of the extraction system and extract them simultaneously with the XAD-2 resin.
- 3.4.5.1.3 Adsorbent Module. Suspend the adsorbent module directly over the extraction thimble in the beaker (see Section 3.4.5.1.1.). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD-2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD-2 glass wool plug to the thimble.
- 3.4.5.1.4 Container No. 2 (Acetone and Methylene Chloride Rinse). Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus, at a temperature of less than 37°C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD-2 resin in the Soxhlet apparatus described in Section 3.4.5.1.1.
- 3.4.5.1.5 Extraction. Add 100  $\mu$ l of the internal standard solution (Section 3.4.3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from Section 3.4.5.1.3. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD-2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and

add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately 2/3 full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in Sections 3.4.5.2 and 3.4.5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

3.4.5.1.6 Container No. 3 (Toluene Rinse). Add 100  $\mu$ L of the Internal Standard solution (Section 3.4.3.3.20) to the contents of the container. Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus at a temperature of less than 37°C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in Sections 3.4.5.2 and 3.4.5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

#### 3.4.5.2 Sample Cleanup and Fractionation.

3.4.5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm x 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (Section 3.4.2.3.8).

- 3.4.5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.
- 3.4.5.2.3 AX-21 Carbon/Celite 545 Column. Remove the bottom 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases, AX-21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50°C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200  $\mu$ l using a stream of N2. Store extracts at room temperature, shielded from light, until the analysis is performed.
- 3.4.5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in Sections 3.4.5.3.1 and 3.4.5.3.2. Immediately prior to analysis, add a  $20-\mu l$  aliquot of the Recovery Standard solution from Table 1 to each sample. A  $2-\mu l$  aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 capillary column to determine the concentration of each isomer of PCDDs and PCDFs (tetra- through octa-). If tetra-chlorinated

dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB-225 column to measure the 2,3,7,8-tetrachlorodibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate, using calibration and performance checks, that the column system is able to meet the specifications of Section 3.4.6.1.2.2.

- 3.4.5.3.1 Gas Chromatograph Operating Conditions.
- 3.4.5.3.1.1 Injector. Configured for capillary column, splitless, 250°C.
  - 3.4.5.3.1.2 Carrier Gas. Helium, 1-2 ml/min.
- 3.4.5.3.1.3 Oven. Initially at 150°C. Raise by at least 40°C/min to 190°C and then at 3°C/min up to 300°C.
  - 3.4.5.3.2 High Resolution Mass Spectrometer.
  - 3.4.5.3.2.1 Resolution. 10000 m/e.
  - 3.4.5.3.2.2 Ionization Mode. Electron impact.
  - 3.4.5.3.2.3 Source Temperature 250°C.
- 3.4.5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.4-2.
- 3.4.5.3.2.5 Identification Criteria, The following identification criteria shall be used for the characterization of polychlorinated dibenzo-dioxins and dibenzofurans.

ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTIONS MASS SPECTROMETRY FOR PCDD's AND PCDF's

Table 3.4-2

Accurate mass	Ion type	Elemental composition	Analyte
292.9825	LOCK	C,F11	PFK
303.9016	М	C <sub>12</sub> H <sub>4</sub> 35C1 <sub>4</sub> O	TCDF
305.8987	M+2	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> C1 <sup>37</sup> O	TCDF
315.9419	М	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> <sup>35</sup> C1 <sub>4</sub> O	TCDF (S)
317.9389	M+2	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> <sup>35</sup> C13 <sup>37</sup> C10	TCDF (S)
319.8965	М	C <sub>12</sub> H <sub>4</sub> 35C1O <sub>2</sub>	TCDD
321.8936	M+2	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> ClO <sub>2</sub>	TCDD
327.8847	М	C <sub>12</sub> H <sub>4</sub> <sup>37</sup> Cl <sub>4</sub> O <sub>2</sub>	TCDD (S)
330.9792	QC	C <sub>7</sub> F <sub>13</sub>	PFK
331.9368	<b>M</b>	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>4</sub> O <sub>2</sub>	TCDD (S)
333.9339	M+2	13C12H435C137C102	TCDD (S)
339.8597	M+2	C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> ClO	PECDF
341.8567	M+4	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl <sub>2</sub> O	PeCDF .
351.9000	M+2	<sup>13</sup> C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> ClO	PeCDF (S)
353.8970	M+4	<sup>13</sup> C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl <sub>2</sub> O	PeCDF (S)
355.8546	M+2	C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> ClO <sub>2</sub>	PeCDD
357.8516	M+4	$C_{12}H_3^{35}Cl_3^{37}Cl_2O_2$	PeCDD
367.8949	M+2	13C12H335C1437C102	PeCDD (S)
369.8919	M+4	<sup>13</sup> C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	PeCDD (S)
375.8364	M+2	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> ClO	HxCDPE
409.7974	M+2	C <sub>12</sub> H <sub>3</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> ClO	HpCPDE
	292.9825 303.9016 305.8987 315.9419 317.9389 319.8965 321.8936 327.8847 330.9792 331.9368 333.9339 339.8597 341.8567 351.9000 353.8970 355.8546 357.8516 367.8949 369.8919 375.8364	292.9825 LOCK 303.9016 M 305.8987 M+2 315.9419 M 317.9389 M+2 319.8965 M 321.8936 M+2 327.8847 M 330.9792 QC 331.9368 M 333.9339 M+2 339.8597 M+2 341.8567 M+4 351.9000 M+2 353.8970 M+4 355.8546 M+2 357.8516 M+4 367.8949 M+2 369.8919 M+4 375.8364 M+2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table 3.4-2 (Continued)

ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF's

Descriptor number	Accurate mass	Ion type	Elemental composition	Analyte
3	373.8208	M+2	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> ClO	HxCDF
	375.8178	M+4	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O	HxCDF
	383.8639	M	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> C1 <sub>6</sub> O	HxCDF (S)
	385.8610	M+2	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> ClO	HxCDF (S)
	389.8157	M+2	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> ClO <sub>2</sub>	HxCDD
	391.8127	M+4	$C_{12}H_2^{35}Cl_4^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C <sub>9</sub> F <sub>15</sub>	PFK
	401.8559	M+2	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> C1 <sub>5</sub> <sup>37</sup> C10 <sub>2</sub>	HxCDD (S)
	403.8529	M+4	<sup>13</sup> C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O	HxCDD (S)
	445.7555	M+4	C <sub>12</sub> H <sub>2</sub> <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> Cl <sub>2</sub> O	OCDPE
	430.9729	QC	C <sub>9</sub> F <sub>17</sub>	PFK
4	407.7818	M+2	C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> ClO	HpCDF
	409.7789	M+4	C <sub>12</sub> H <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl <sub>2</sub> O	HpCDF
	417.8253	н	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>7</sub> O	HpCDF (S)
	419.8220	M+2	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> ClO	HpCDF (S)
	423.7766	M+2	C <sub>12</sub> H <sup>35</sup> Cl <sub>6</sub> <sup>37</sup> ClO <sub>2</sub>	HPCDD
	425.7737	M+4	C <sub>12</sub> H <sup>35</sup> Cl <sub>3</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HpCDD
	435.8169	M+2 •	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> C1 <sub>6</sub> <sup>37</sup> C1O <sub>2</sub>	HpCDD (S)

Table 3.4-2 (Continued)

ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF's

Descriptor number	Accurate mass	Ion type	Elemental composition	Analyte
	437.8140	M+4	<sup>13</sup> C <sub>12</sub> H <sup>35</sup> Cl <sub>5</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HpCDD (S)
	479.7165	M+4	C <sub>12</sub> H <sup>35</sup> Cl <sub>7</sub> <sup>37</sup> Cl <sub>2</sub> O	NCPDE
	430.9729	LOCK	C <sub>9</sub> F <sub>17</sub>	PFK
	441.7428	M+2	C <sub>12</sub> 35Cl,37ClO	OCDF
	443.7399	M+4	C <sub>12</sub> 35Cl <sub>6</sub> 37Cl <sub>2</sub> O	OCDF
	457.7377	M+2	C <sub>12</sub> 35Cl, <sup>37</sup> ClO <sub>2</sub>	OCDD
	459.7348	M+4	C <sub>12</sub> 35Cl <sub>6</sub> 37Cl <sub>2</sub> O <sub>2</sub>	OCDD
	469.77 <b>79</b>	M+2	13C <sub>12</sub> 35Cl <sub>7</sub> 37ClO <sub>2</sub>	OCDD (S)
	471.7750	M+4	13C <sub>12</sub> 35Cl <sub>6</sub> 37Cl <sub>2</sub> O <sub>2</sub>	OCDD (S)
	513.6775	M+4	C <sub>12</sub> 35Cl <sub>8</sub> 37Cl <sub>2</sub> O <sub>2</sub>	DCDPE
	442.9728	QC	C <sub>10</sub> F <sub>1</sub> ,	PFK

a) The following nuclidic masses were used:

H = 1.007825 O = 15.994915 C = 12.000000  $^{35}C1 = 34.968853$  $^{13}C = 13.003355$   $^{37}C1 = 36.965903$ 

F = 18.9984

QC - Ion selected for monitoring instrument stability during the GC/MS analysis

S - Labeled Standard

Table 3.4-3 ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD's AND PCDF's

Number of Chlorine	Ion	Theoretical	Control limits			
atoms	type	ratio	Lower	Upper		
4	M/M+2	0.77	0.65	0.89		
5	M+2/M+4	1.55	1.32	1.78		
6	M+2/M+4	1.24	1.05	1.43		
64	M/M+2	0.51	0.43	0.59		
7 <sup>b</sup>	M/M+2	0.44	0.37	0.51		
7	M+2/M+4	1.04	0.88	1.20		
8	M+2/M+4	0.89	0.76	1.02		

a) Used only for <sup>13</sup>C-HxCDF b) Used only for <sup>13</sup>C-HpCDF

- 1. The integrated ion-abundance ratio (M/M+2 or M+2/M+4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 3.
- 2. The retention time for the analytes must be within 3 seconds of the corresponding <sup>13</sup>C-labeled internal standard, surrogate or alternate standard.
- 3. The monitored ions, shown in Table 3.4-2 for a given analyte, shall reach their maximum within 2 seconds of each other.
- 4: The identification of specific isomers that do not have corresponding <sup>13</sup>C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRTs found in the continuing calibration.
- 5. The signal to noise ratio for all monitored ions must be greater than 2.5.
- 6. The confirmation of 2,3,7,8-TCDD and 2,3,7,8-TCDF shall satisfy all of the above identification criteria.
- 7. For the identification of PCDFs, no signal may be found in the corresponding PCDPE channels.
- 3.4.5.3.2.6 Quantitation. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantitate the indigenous PCDDs or PCDFs in its homologous series. For example, the  $^{13}C_{12}$ -2,3,7,8-tetrachlorodibenzodioxin is used to calculate the concentrations of all other tetrachlorinated isomers. Recoveries of the tetra- and penta-internal standards are calculated using the  $^{13}C_{12}$ -1,2,3,4-TCDD. Recoveries of the hexa- through octa- internal standards are calculated using  $^{13}C_{12}$ -1,2,3,7,8,9-HxCDD.

Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

## 3.4.6 <u>Calibration</u>

Same as Method 5 with the following additions.

- 3.4.6.1 GC/MS System.
- 3.4.6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 3.4-4. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 4) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 3.4-5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 3.
  - 3.4.6.1.2 Daily Performance Check.
- 3.4.6.1.2.1 Calibration Check. Inject one  $\mu l$  of solution Number 3 from Table 4. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRFs for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 3.4-5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 3.4-3.
- 3.4.6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDDs and PCDFs that documents resolution between 2,3,7,8-TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Table 3.4-4

COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

COMPOSITION OF	THE INITIAL CA						
		•	Concent	rations	(pg/μL)		
Compound	Solution No.	1	2	3	4	5	
Unlabeled Analytes							
				_	5.0	1.00	
2,3,7,8-TCDD		0.5 0.5	1 1	5 5	50 50	100 100	
2,3,7,8-TCDF		2.5	5	25	250	500	
1,2,3,7,8-PeCDD 1,2,3,7,8-PeCDF		2.5	5	25	250	500	
2,3,4,7,8-PeCDF		2.5	5	25	250	500	
1,2,3,4,7,8-HxCDD		2.5	5	25	250	500	
1,2,3,6,7,8-HxCDD		2.5	5	25	250	500	
1,2,3,7,8,9-HxCDD		2.5	5 5	25	250	500	
1,2,3,4,7,8-HxCDF		2.5		25	250	500	
1,2,3,6,7,8-HxCDF		2.5	5 5	25 25	250 250	500 500	
1,2,3,7,8,9-HxCDF		2.5 2.5	5	25	250	500	
2,3,4,6,7,8-HxCDD 1,2,3,4,6,7,8-HpCDD		2.5	5	25	250	500	
1,2,3,4,6,7,8-HpCDF		2.5	5	25	250	500	
1,2,3,4,7,8,9-HpCDF		2.5	5	25	250	500	
OCDD		5.0	10	50	500	1000	
OCDF		5.0	10	50	500	1000	
Internal Standards	•						
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD		100	100	100	100	100	
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD		100	100	100	100	100	
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD		100	100	100	100	100	
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD		100	100	100	100	100	
13C12-OCDD		200	200	200	200	200	
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF		100	100	100	100	100	
13C <sub>12-</sub> 1,2,3,7,8-PeCDF		100 100	100 100	100 100	100 100	100 100	
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDF <sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF		100	100	100	100	100	
0 <sub>12</sub> -1,2,5,4,0,7,0-npobr		100	100	100	200	200	
Surrogate Standards	Surrogate Standards						
<sup>37</sup> C1,-2,3,7,8-TCDD		0.5	5 1	5	50	100	
<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF		2.5		25	250	500	
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD		2.5		25	250	500	
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF		2.5		25	250	500	
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF		2.5	5 5	25	250	500	

Table 3.4-4 (Continued)

COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

	Concentrations (pg						
Compound	Solution No.	1	2	3	4	5	
Alternative Standard  13C <sub>12</sub> -1,2,3,7,8,9-HxCDF		2.5	5	25	250	500	
Recovery Standards  13C <sub>12</sub> -1,2,3,4-TCDD 13C <sub>12</sub> -1,2,3,7,8,9-HxCDD		100 100	100 100	100 100	100 100	100 100	

Table 3.4-5

MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

	Relative Resp	onse Factors
Compound	Initial Calibration RSD	Daily Calibration % Difference
Unlabeled Analytes		
2,3,7,8-TCDD 2,3,7,8-TCDF 1,2,3,7,8-PeCDD 1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF 1,2,4,5,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,4,7,8,9-HxCDD 1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HyCDD 1,2,3,4,6,7,8-HpCDD 0CDD 0CDF	25 25 25 25 25 25 25 25 25 25 25 25 25 2	25 25 25 25 25 25 25 25 25 25 25 25 25 2
Internal Standards		
13C <sub>12</sub> -2,3,7,8-TCDD 13C <sub>12</sub> -1,2,3,7,8-PeCCD 13C <sub>12</sub> -1,2,3,6,7,8-HxCDD 13C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD 13C <sub>12</sub> -0CDD	25 30 25 30 30	25 30 25 30 30
13C <sub>12</sub> -2,3,7,8-TCDF 13C <sub>12</sub> -1,2,3,7,8-PeCDF 13C <sub>12</sub> -1,2,3,6,7,8-HxCDF 13C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	30 30 30 30	30 30 30 30
<u>Surrogate Standards</u>		
37Cl <sub>4</sub> -2,3,7,8-TCDD 13C <sub>12</sub> -2,3,4,7,8-PeCDF 13C <sub>12</sub> -1,2,3,4,7,8-HxCDD 13C <sub>12</sub> -1,2,3,4,7,8-HXCDF 13C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	25 25 25 25 25	25 25 25 25 25
Alternate Standard  13C <sub>12</sub> -1,2,3,7,8,9-HxCDF	25	25

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8-TCDF and other TCDF isomers.

3.4.6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3.4-3. Monitor the quality control check channels specified in Table 3.4-3 to verify instrument stability during the analysis.

## 3.4.7 <u>Quality Control</u>

- 3.4.7.1 Sampling Train Collection Efficiency Check. Add 100  $\mu$ l of the surrogate standards in Table 3.4-1 to the adsorbent cartridge of each train before collecting the field samples.
- 3.4.7.2 Internal Standard Percent Recoveries. A group of nine carbon-labeled PCDDs and PCDFs representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantitate the native PCDDs and PCDFs present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetrathrough hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.
- 3.4.7.3 Surrogate Recoveries. The five surrogate compounds in Table 3.4-4 are added to the resin the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDDs and PCDFs. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of samples.

3.4.7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

### 3.4.8 Quality Assurance

- 3.4.8.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.
- 3.4.8.2 Audit Procedure. Analyze an audit sample with each set of compliance samples. The audit sample contains tetra through octa isomers of PCDD and PCDF. Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit sample.
- 3.4.8.3 Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing:

Source Test Audit Coordinator (MD-77B)
Quality Assurance Division
Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

3.4.8.4 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency and a second copy to the STAC. The EPA Regional office or the

appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

## 3.4.9 Calculations

Same as Method 5, Section 6 with the following additions.

#### 3.4.9.1 Nomenclature.

- A<sub>ai</sub> Integrated ion current of the noise at the retention time of the analyte.
- A integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.
- A<sub>eij</sub> Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.
- A cij Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.
- A<sub>csi</sub> = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.
- A<sub>i</sub> = Integrated ion current of the two ions characteristic of compound in the sample.
- A' Integrated ion current of the two ions characteristic of internal standard i in the sample.
- A<sub>rs</sub> Integrated ion current of the two ions characteristic of the recovery standard.
- A<sub>si</sub> = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.
- $C_i$  Concentration of PCDD or PCDF i in the sample,  $pg/M^3$ .
- C<sub>T</sub> Total concentration of PCDDs or PCDFs in the sample, pg/M<sup>3</sup>.
- m<sub>ci</sub> = Mass of compound i in the calibration standard injected into the analyzer, pg.
- m\*ci = Mass of labeled compound i in the calibration standard injected into the analyzer, pg.
- m'; Mass of internal standard i added to the sample, pg.

m<sub>rs</sub> = Mass of recovery standard in the calibration standard injected into the analyzer, pg.

 $m_{si}$  - Mass of surrogate compound i in the calibration standard, pg.

RRF, = Relative response factor.

RRF<sub>rs</sub> - Recovery standard response factor.

RRF = Surrogate compound response factor.

## 3.4.9.2 Average Relative Response Factor.

$$RRF_{i} = 1/n \sum_{j=1}^{n} [A_{cij}m_{ci}^{*}/(A_{cij}^{*}m_{ci})]$$
 Eq. 23-1

3.4.9.3 Concentration of the PCDDs and PCDFs.

$$C_i = m^*_i A_i / (A^*_i RRF_i V_{m(std)})$$
 Eq. 23-2

3.4.9.4 Recovery Standard Response Factor.

$$RRF_{rs} - A_{ci}^* m_{rs}/(A_{rs} m_{ci}^*)$$
 Eq. 23-3

3.4.9.5 Recovery of Internal Standards (R\*).

$$R^* - (A_i^* m_{rs} / A_{rs} RF_{rs} m_i^*) \times 100$$
 Eq. 23-4

3.4.9.6 Surrogate Compound Response Factor.

RRFs = 
$$A_{ci}^* m_s / (A_{cis} m_{ci}^*)$$
 Eq. 23-5

3.4.9.7 Recovery of Surrogate Compounds  $(R_a)$ .

$$R_{x} = (A_{x} m_{x}^{*} / A_{x}^{*} RRF_{x} m_{x}) \times 100$$
 Eq. 23-6

3.4.9.8 Minimum Detectable Limit (MDL).

$$MDL = 2.5 A_{ai} m_{i}^{*}/(A_{ci}^{*} RRF_{i})$$
 Eq. 23-7

3.4.9.9 Total Concentration of PCDDs and PCDFs in the Sample.

$$C_{T} = \sum_{i=1}^{n} C_{i}$$
 Eq. 23-8

## 3.4.10 Bibliography

- 1. American Society of Mechanical Engineers. Sampling for the Determination of Chlorinated Organic Compounds in Stack Emissions. Prepared for U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, D.C. December 1984. 25 p.
- 2. American Society of Mechanical Engineers. Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF). Prepared for the U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, D.C. December 1984. 23 p.
- 3. Thompson, J.R. (ed.) Analysis of Pesticide Residues in Human and Environmental Samples. U.S. Environmental Protection Agency. Research Triangle Park, NC. 1974.
- 4. Triangle Laboratories. Case Study: Analysis of Samples for the Presence of Tetra Through Octachloro-p-Dibenzodioxins and Dibenzofurans. Research Triangle Park, NC. 1988. 26 p.
- 5. U.S. Environmental Protection Agency. Draft Method 8290 The Analysis of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofurans by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry. In: Test Methods for Evaluating Solid Waste. Washington, D.C. SW-846.

3.5 Sampling for Aldehyde and Ketone Emissions from Stationary Sources
(Method 0011)

### 3.5.1 Scope and Application

This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of formaldehyde, CAS Registry number 50-00-0, and possibly other aldehydes and ketones from stationary sources as specified in the regulations. The methodology has been applied specifically to formaldehyde; however, many laboratories have extended the application to other aldehydes and ketones. Compounds derivatized with 2,4-dinitrophenyl-hydrazine can be detected as low as  $6.4 \times 10^{-8}$  lbs/cu ft (1.8 ppbv) in stack gas over a 1 hr sampling period, sampling approximately 45 cu ft.

## 3.5.2 <u>Summary of Method</u>

3.5.2.1 Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in aqueous acidic 2,4-dinitrophenyl-hydrazine. Formaldehyde present in the emissions reacts with the 2,4-dinitrophenyl-hydrazine to form the formaldehyde dinitrophenylhydrazone derivative. The dinitrophenylhydrazone derivative is extracted, solvent-exchanged, concentrated, and then analyzed by high performance liquid chromatography.

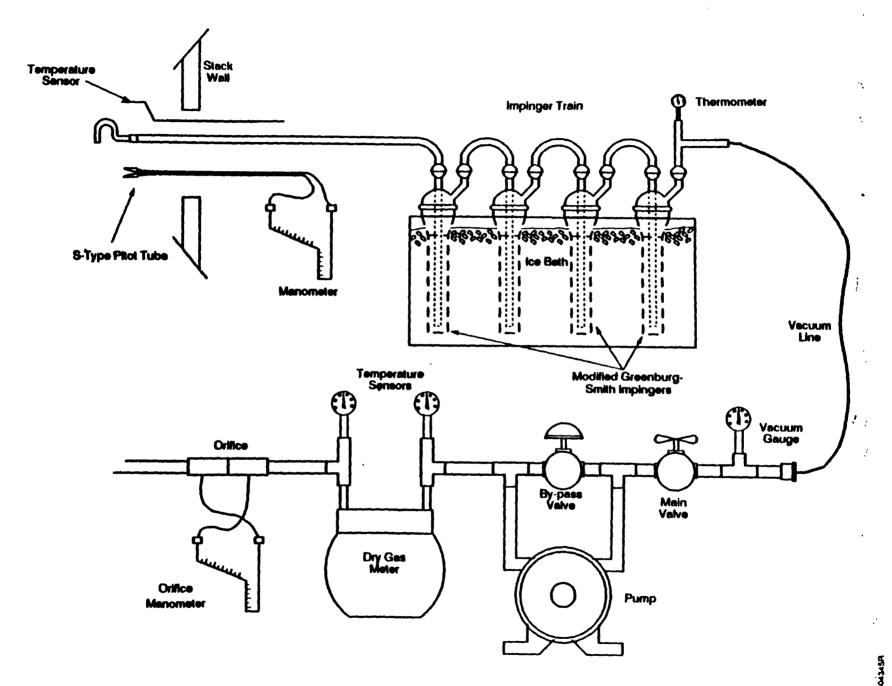
## 3.5.3 Interferences

3.5.3.1 A decomposition product of 2,4-dinitrophenyl-hydrazine, 2,4-dinitroaniline, can be an analytical interferant if concentrations are high. 2,4-Dinitroaniline can coelute with 2,4-dinitrophenylhydrazone of formaldehyde under high performance liquid chromatography conditions, which may be used for the analysis. High concentrations of highly-oxygenated compounds, especially acetone, that have the same retention time or nearly the same retention time as the dinitrophenylhydrazone of formaldehyde, and that also absorb at 360 nm, will interfere with the analysis.

Formaldehyde, acetone, and 2,4-dinitroaniline contamination of the aqueous acidic 2,4-dinitrophenyl-hydrazine (DNPH) reagent is frequently encountered. The reagent must be prepared within five days of use in the field and must be stored in an uncontaminated environment both before and after sampling in order to minimize blank problems. Some concentration of acetone contamination is unavoidable, because acetone is ubiquitous in laboratory and field operations. However, the acetone contamination must be minimized.

### 3.5.4 Apparatus and Materials

- 3.5.4.1 A schematic of the sampling train is shown in Figure 3.5-1. This sampling train configuration is adapted from EPA Method 4 procedures. The sampling train consists of the following components: Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Metering System, Barometer, and Gas Density Determination Equipment.
- 3.5.4.1.1 Probe Nozzle: Quartz or glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant inner diameter. The nozzle shall be buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.15 cm(1/16 in), e.g., 0.32 to 1.27 cm (1/8 to 1/2 in), of larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Section 3.5.8.1
- 3.5.4.1.2 Probe Liner: Borosilicate glass or quartz shall be used for the probe liner. The tester should not allow the temperature in the probe to exceed  $120 \pm 14^{\circ}C$  (248  $\pm$  25°F).
- 3.5.4.1.3 Pitot Tube: The Pitot tube shall be Type S, as described in Section 2.1 of EPA Method 2, or any other appropriate device. The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plan (see EPA Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2.



Formaldehyde Sampling Train

Figure 3.5-1

- 3.5.4.1.4 Differential Pressure Gauge: The differential pressure gauge shall be an inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2. One manometer shall be used for velocity-head reading and the other for orifice differential pressure readings.
- 3.5.4.1.5 Impingers: The sampling train requires a minimum of four impingers, connected as shown in Figure 3.5-1, with ground glass (or equivalent) vacuum-tight fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm inside diameter (1/2 in) glass tube extending to 1.3 cm (1/2 in) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip. Place a thermometer capable of measuring temperature to within 1°C (2°F) at the outlet of the fourth impinger for monitoring purposes.
- 3.5.4.1.6 Metering System: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature within 3°C (5.4°F), dry-gas meter capable of measuring volume to within 1%, and related equipment as shown in Figure 3.5-1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry gas meter should have a recording capacity of 0-999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems may be used which are capable of maintaining sample volumes to within 2%. The metering system may be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.
- 3.5.4.1.7 Barometer: The barometer may be mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service Station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increases (vice versa for elevation decrease).
- 3.5.4.1.8 Gas Density Determination Equipment: Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.3 of EPA Method 2), and

gas analyzer, if necessary (as described in EPA Method 3). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot openings (see EPA Method 2, Figure 2-7). As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

## 3.5.4.2 Sample Recovery

- 3.5.4.2.1 Probe Liner: Probe nozzle and brushes; Teflon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the impingers.
- 3.5.4.2.2 Wash Bottles: Three wash bottles are required. Teflon or glass wash bottles are recommended; polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.
- 3.5.4.2.3 Graduate Cylinder and/or Balance: A graduated cylinder or balance is required to measure condensed water to the nearest 1 ml or 1 g. Graduated cylinders shall have division not >2 ml. Laboratory balances capable of weighing to ±0.5 g are required.
- 3.5.4.2.4 Amber Glass Storage Containers: One-liter wide-mouth amber flint glass bottles with Teflon-lined caps are required to store impinger water samples. The bottles must be sealed with Teflon tape.

3.5.4.2.5 Rubber Policeman and Funnel: A rubber policeman and funnel are required to aid in the transfer of material into and out of containers in the field.

## 3.5.4.3 Reagent Preparation

- 3.5.4.3.1 Bottles/Caps: Amber 1- or 4-L bottles with Teflon-lined caps are required for storing cleaned DNPH solution. Additional 4-L bottles are required to collect waste organic solvents.
- 3.5.4.3.2 Large Glass Container: At least one large glass (8 to 16 L) is required for mixing the aqueous acidic DNPH solution.
- 3.5.4.3.3 Stir Plate/Large Stir Bars/Stir Bar Retriever: a magnetic stir plate and large stir bar are required for the mixing of aqueous acidic DNPH solution. A stir bar retriever is needed for removing the stir bar from the large container holding the DNPH solution.
- 3.5.4.3.4 Buchner Filter/Filter Flask/Filter Paper: A large filter flask (2-4 L) with a buchner filter, appropriate rubber stopper, filter paper, and connecting tubing are required for filtering the aqueous acidic DNPH solution prior to cleaning.
- 3.5.4.3.5 Separatory Funnel: At least one large separatory funnel (2 L) is required for cleaning the DNPH prior to use.
- 3.5.4.3.6 Beakers: Beakers (150 ml, 250 ml, and 400 ml) are useful for holding/measuring organic liquids when cleaning the aqueous acidic DNPH solution and for weighing DNPH crystals.
- 3.5.4.3.7 Funnels: At lease one large funnel is needed for pouring the aqueous acidic DNPH into the separator funnel.

- 3.5.4.3.8 Graduated Cylinders: At least one large graduated cylinder (1 to 2 L) is required for measuring organic-free reagent water and acid when preparing the DNPH solution.
- 3.5.4.3.9 Top-Loading Balance: A one-place top loading balance is needed for weighing out the DNPH crystals used to prepare the aqueous acidic DNPH solution.
- 3.5.4.3.10 Spatulas: Spatulas are needed for weighing out DNPH when preparing the aqueous DNPH solution.
- 3.5.4.4 Crushed Ice: Quantities ranging from 10-50 lb may be necessary during a sampling run, depending upon ambient temperature. Samples which have been taken must be stored and shipped cold; sufficient ice for this purpose must be allowed.

## 3.5.5 Reagents

- 3.5.5.1 Reagent grade chemicals shall be used in all tests.
  Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 3.5.5.2 Organic-free reagent water: All references to water in this method refer to organic-free reagent water, as defined in Chapter One.
- 3.5.5.3 Silica Gel: Silica gel shall be indicating type, 6-16 mesh. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

- 3.5.5.4 2,4-dinitrophenylhydrazine (DNPH),  $[2,4-(O_2N)_2C_6H_3]NHNH_2$  The quantity of water may vary from 10 to 30%.
- 3.5.5.4.1 The 2,4-dinitrophenylhydrazine reagent must be prepared in the laboratory within five days of sampling use in the field. Preparation of DNPH can also be done in the field, with consideration of appropriate procedures required for safe handling of solvent in the field. When a container of prepared DNPH reagent is opened in the field, the contents of the opened container should be used within 48 hours. All laboratory glassware must be washed with detergent and water and rinsed with water, methanol, and methylene chloride prior to use.

NOTE: DNPH crystals or DNPH solution should be handled with plastic gloves at all times with prompt and extensive use of running water in case of skin exposure.

3.5.5.4.2 Preparation of Aqueous Acidic DNPH Derivatizing Reagent: Each batch of DNPH reagent should be prepared and purified within five days of sampling, according to the procedures described below.

NOTE: Reagent bottles for storage of cleaned DNPH derivatizing solution must be rinsed with acetonitrile and dried before use. Baked glassware is not essential for preparation of DNPH reagent. The glassware must not be rinsed with acetone or an unacceptable concentration of acetone contamination will be introduced. If field preparation of DNPH is performed, caution must be exercised in avoiding acetone contamination.

3.5.5.4.2.1 Place an 8 L container under a fume hood on a magnetic stirrer. Add a large stir bar and fill the container half full of organic-free reagent water. Save the empty bottle from the organic-free reagent water. Start the stirring bar and adjust the stir rate to be as fast as possible. Using a graduated cylinder, measure 1.4 ml of concentrated hydrochloric acid. Slowly pour the acid into the stirring water. Fumes may be generated and the water may become warm. Weight the DNPH crystals on a

one-place balance (see Table 3.5-1 for approximate amounts) and add to the stirring acid solution. Fill the 8-L container to the 8-L mark with organic-free reagent water and stir overnight. If all of the DNPH crystals have dissolved overnight, add additional DNPH and stir for two more hours. Continue the process of adding DNPH with additional stirring until a saturated solution has been formed. Filter the DNPH solution using vacuum filtration. Gravity filtration may be used, but a much longer time is required. Store the filtered solution in an amber bottle at room temperature.

- 3.5.5.4.2.2 Within five days of proposed use, place about 1.6 L of the DNPH reagent in a 2-L separatory funnel. Add approximately 200 ml of methylene chloride and stopper the funnel. Wrap the stopper of the funnel with paper towels to absorb any leakage. Invert and vent the funnel. Then shake vigorously for 3 minutes. Initially, the funnel should be vented frequently (every 10 -15 sec). After the layers have separated, discard the lower (organic) layer.
- 3.5.5.4.2.3 Extract the DNPH a second time with methylene chloride and finally with cyclohexane. When the cyclohexane layer has separated from the DNPH reagent, the cyclohexane layer will be the top layer in the separatory funnel. Drain the lower layer (the cleaned extract DNPH reagent solution) into an amber bottle that has been rinsed with acetonitrile and allowed to dry.
- 3.5.5.4.3 Quality Control: Take two aliquots of the extracted DNPH reagent. The size of the aliquots is dependent upon the exact sampling procedure used, but 100 ml is reasonably representative. To ensure that the background in the reagent is acceptable for field use, analyze one aliquot of the reagent according to the procedure of Method 8315. Save the other aliquot of aqueous acidic DNPH for use as a method blank when the analysis is performed.
- 3.5.5.4.4 Shipment to the Field: Tightly cap the bottle containing extracted DNPH reagent using a Teflon-lined cap. Seal the bottle with Teflon

# APPROXMIATE AMOUNT OF CRYSTALLINE DNPH USED TO PREPARE A SATURATED SOLUTION

Amount of Moisture in DNPH	Weight Required per 8 L of Solution
10 weight percent	31 g
15 weight percent 30 weight percent	33 g 40 g
30 weight percent	40 g

Table 3.5-2

# INSTRUMENT DETECTION LIMITS AND REAGENT CAPACITY FOR FORMALDEHYDE ANALYSIS<sup>1</sup>

Analyte	Detection Limit, ppbv <sup>2</sup>	Reagent Capacity, ppm			
Formaldehyde	1.8	66			
Acetaldehyde	1.7	70			
Acrolein	1.5	75			
Acetone/Propionaldehyde	1.5	75			
Butyraldehyde	1.5	79			
Methyl ethyl ketone	1.5	79			
Valeraldehyde	1.5	84			
Isovaleraldehyde	1.4	84			
Hexaldehyde	1.3	88			
Benzaldehyde	1.4	84			
o-/m-/p-Tolualdehyde	1.3	89			
Dimethylbenzaldehyde	1.2	93			

<sup>&</sup>lt;sup>1</sup>Oxygenated compounds in addition to formaldehyde are included for comparison with formaldehyde; extension of the methodology to other compounds is possible.

<sup>&</sup>lt;sup>2</sup>Detection limits are determined in solvent. These values therefore represent the optimum capability of the methodology.

tape. After the bottle is labeled, the bottle may be placed in a friction-top can (paint can or equivalent) containing a 1-2 inch layer of granulated charcoal and stored at ambient temperature until use.

- 3.5.5.4.4.1 If the DNPH reagent has passed the Quality Control criteria, the reagent may be packaged to meet necessary shipping requirements and sent to the sampling area. If the Quality Control criteria are not met, the reagent solution may be re-extracted or the solution may be re-prepared and the extraction sequence repeated.
- 3.5.5.4.4.2 If the DNPH reagent is not used in the field within five days of extraction, an aliquot may be taken and analyzed as described in Method 0011A. If the reagent meets the Quality Control requirements, the reagent may be used. If the reagent does not meet the Quality Control requirements, the reagent must be discarded and new reagent must be prepared and tested.
- 3.5.5.4.5 Calculation of Acceptable Concentrations of Impurities in DNPH Reagent: The acceptable impurity concentration (AIC,  $\mu g/ml$ ) is calculated from the expected analyte concentration in the sampled gas (EAC, ppbv), the volume of air that will be sampled at standard conditions (SVOL, L), the formula weight of the analyte (FW, g/mol), and the volume of DNPH reagent that will be used in the impingers (RVOL, ml):

AIC =  $0.1 \times [EAC \times SVOL \times FW/22.4 \times (FW + 180)/FW](RVOL \times 1,000)$ 

## where:

- 0.1 is the acceptable contaminant concentration.
- 22.4 is a factor relating ppbv to g/L,
- 180 is a facto relating underivatized to derivatized analyte
- 1,000 is a unit conversion factor.
- 3.5.5.4.6 Disposal of Excess DNPH Reagent: Excess DNPH reagent may be returned to the laboratory and recycled or treated as aqueous waste for

disposal purposes. 2,4-dinitrophenylhydrazine is a flammable solid when dry, so water should not be evaporated from the solution of the reagent.

- 3.5.5.5 Field Spike Standard Preparation: To prepare a formaldehyde field spiking standard at 4.01 mg/ml, use a 500  $\mu$ l syringe to transfer 0.5 ml to 37% by weight of formaldehyde (401 mg/ml) to a 50 ml volumetric flask containing approximately 50 ml of methanol. Dilute to 50 ml with methanol.
- 3.5.5.6 Hydrochloric Acid, HCL: Reagent grade hydrochloric acid (approximately 12N) is required for acidifying the aqueous DNPH solution.
- 3.5.5.7 Methylene Chloride, CH<sub>2</sub>Cl<sub>2</sub>: Methylene chloride (suitable for residue and pesticide analysis, GC/MS, HPLC, GC, Spectrophotometry or equivalent) is required for cleaning the aqueous acidic DNPH solution, rinsing glassware, and recovery of sample trains.
- 3.5.5.8 Cyclohexane,  $C_6H_{12}$ : Cyclohexane (HPLC grade) is required for cleaning the aqueous acidic DNPH solution.
- NOTE: Do not use spectroanalyzed grades of cyclohexane if this sampling methodology is extended to aldehydes and ketones with four or more carbon atoms.
- 3.5.5.9 Methanol, CH<sub>3</sub>OH: Methanol (HPLC grade or equivalent) is required for rinsing glassware.
- 3.5.5.10 Acetonitrile, CH $_3$ CN: Acetonitrile (HPLC grade or equivalent) is required for rinsing glassware.
- 3.5.5.11 Formaldehyde, HCHO: Analytical grade or equivalent formaldehyde is required for preparation of standards. If other aldehydes or ketones are used, analytical grade or equivalent is required.

## 3.5.6 Sample Collection, Preservation, and Handling

3.5.6.1 Because of the complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

## 3.5.6.2 Laboratory Preparation:

- 3.5.6.2.1 All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified.
- 3.5.6.2.2 Weigh several 200 to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger or sampling holder just prior to train assembly.

### 3.5.6.3 Preliminary Field Determinations:

- 3.5.6.3.1 Select the sampling site and the minimum number of sampling point according to EPA Method 1 or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. A leak-check of the pitot lines according to EPA Method 2, Section 3.1, must be performed. Determine the stack gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack gas dry molecular weight, as described in EPA Method 2, Section 3.6. If integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.
- 3.5.6.3.2 Select a nozzle size based on the range of velocity heads so that is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 L/min (1.0 cfm). During the run, do not

change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2. of EPA Method 2).

- 3.5.6.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.
- 3.5.6.3.4 A minimum of 45 ft<sup>3</sup> of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of formaldehyde from incineration systems (45 ft<sup>3</sup> is equivalent to one hour of sampling at 0.75 dscf). Additional sample volume shall be collected as necessitated by the capacity of the DNPH reagent and analytical detection limit constraints. To determine the minimum sample volume required, refer to sample calculations in Section 10.
- 3.5.6.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus 0.5 min.
- 3.5.6.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-volume samples. In these cases, careful documentation must be maintained in order to allow accurate calculation of concentrations.

## 3.5.6.4 Preparation of Collection Train:

3.5.6.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon film or aluminum foil until just prior to assembly or until sampling is about to begin.

- 3.5.6.4.2 Place 100 ml of cleaned DNPH solution in each of the first two impingers, and leave the third impinger empty. If additional capacity is required for high expected concentrations of formaldehyde in the stack gas, 200 ml of DNPH per impinger may be used or additional impingers may be used for sampling. Transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the fourth impinger. Care should be taken to ensure that the silica gel is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place or later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.
- 3.5.6.4.3 With a glass or quartz liner, install the selected nozzle using a Viton-A O-ring with stack temperatures are <260°C (500°F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 (Rom, 1972) for details. Other connection systems utilizing either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.
- 3.5.6.4.4 Assemble the train as shown in Figure 3.5-1. During assembly, do not use any silicone grease on ground-glass joints upstream of the impingers. Use Teflon tape, if required. A very light coating of silicone grease may be used on ground-glass joints downstream of the impingers, but the silicone grease should be limited to the outer portion (see APTD-0576) of the ground-glass joints to minimize silicone grease contamination. If necessary, Teflon tape may be used to seal leaks. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperatures.
  - 3.5.6.4.5 Place crushed ice all around the impingers.
- 3.5.6.4.6 Turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to stabilize.

3.5.6.5 Leak-Check Procedures:

#### 3.5.6.5.1 Pre-test Leak Check

3.5.6.5.1.1 After the sampling train has been assembled, turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to stabilize. If a Viton-A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak check the train at the sampling site by plugging the nozzle and pulling a 381 mm Hg (15 in Hg) vacuum.

NOTE: A lower vacuum may be used, provided that the lower vacuum is not exceeded during the test.

- 3.5.6.5.1.2 If an asbestos string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first attaching a carbon-filled leak check impinger to the inlet and then plugging the inlet and pulling a 381 mm Hg (15 in Hg) vacuum. (A lower vacuum any be used if this lower vacuum is not exceeded during the test.) Next connect the probe to the train and leak-check at about 25 mm Hg (1 in Hg) vacuum. Alternatively, leak-check the probe with the rest of the sampling train in one step at 381 mm Hg (15 in Hg) vacuum. Leakage rates in excess of (a) 4% of the average sampling rate or (b) >0.00057 m³/min (0.02 cfm), are unacceptable.
- 3.5.6.5.1.3 The following leak check instructions for the sampling train descried in ADPT-0576 and APTD-0581 may be helpful. Start the pump with the fine-adjust valve fully open and coarse-valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine-adjust valve, as liquid will back up into the train. If the desired vacuum is exceeded, either perform the leak check at this higher vacuum or end the leak check, as shown below, and start over.

3.5.6.5.1.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe. When the vacuum drops to 127 mm (5 in) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed to prevent the liquid in the impingers from being forced backward in the sampling line and silica gel from being entrained backward into the third impinger.

## 3.5.6.5.2 Leak Checks During Sampling Run:

3.5.6.5.2.1 If, during the sampling run, a component change (i.e., impinger) becomes necessary, a leak check shall be conducted immediately after the interruption of sampling and before the change is made. The leak check shall be done according to the procedure described in Section 3.5.6.5.1, except that is shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm or 4% of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester must void the sampling run.

NOTE: Any correction of the sample volume by calculation reduces the integrity of the pollutant concentration data generated and must be avoided.

3.5.6.5.2.2 Immediately after a component change and before sampling is reinitiated, a leak check similar to a pre-test leak check must also be conducted.

### 3.5.6.5.3 Post-test Leak Check:

3.5.6.5.3.1 A leak check is mandatory at the conclusion of each sampling run. The leak check shall be done with the same procedures as the pre-test leak check, except that the post-test leak check shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057

 $m^3/min$  (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall record the leakage rate and void the sampling run.

## 3.5.6.6 Sampling Train Operation:

- 3.5.6.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, below 20 L/min (1.0 cfm). Maintain a temperature around the probe of  $120^{\circ}$ C ( $248^{\circ} \pm 25^{\circ}$ F).
- 3.5.6.6.2 For each run, record the data on a data sheet such as the one shown in Figure 3.5-2. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings required by Figure 2 at least once at each sample point during each time increment and additional readings when significant adjustments 20% variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.
- 3.5.6.6.3 Clean the stack access ports prior to the test run to eliminate the change of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot tube coefficient is  $0.84 \pm 0.02$  and the stack gas equivalent density (dry molecular weight) is equal to  $29 \pm 4$ . APTD-0576 details the procedure for using the nomographs. If the stack gas molecular weight and the pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations.

Plant			Ambient Temperature
Location	<b>1</b>	)	Barometric Pressure
Operator	·		Assumed Moisture %
Dele			Probe Length, m(ft)
Run No			Nozzle Identification No.
Semple Box No.			Average Calibrated Nozzle Diameter, cm (ln)
Meter Box No.			Probe Heating Setting
Meter H@			Leak Rate, m³/min. (cfm)
C Factor			Probe Liner Meterial
Pilot Tube Coefficient Cp	Schematic of Stack Cross Section		Static Pressure, mm Hg (In. Hq)
			Filter No.

		Stack	Velocity Head	Pressure Differential Across Orifice		Gas Sample Temp. at Dry Gas Meter			Temperature of Gas Leaving	
Traverse Point Number	Sempling Time (0) Min.	Vecuum mm Hg (In. Hg)	Temperature (T <sub>r</sub> ) °C ("F)	Head (P <sub>s</sub> ) mm (In) H <sub>s</sub> O	Meter mm (H <sub>2</sub> O) (in H <sub>2</sub> O)	Gas Sample Volume m³ (ft³)	Inlet *C(*F)	Outlet *C(*F)	Filter Holder Temperature °C(°F)	Last Impinger *C(*F)
							<del></del>			
								<del></del>		
					<u> </u>					·
Total							Avg.	Avg.		
Average -										

Figure 3.5-2 Field Data Sheet

- 3.5.6.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack in order to prevent liquid from backing up through the train. If necessary, the pump may be turned on with the coarse-adjust valve closed.
- 3.5.6.6.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.
- 3.5.6.6.6 Traverse the stack cross section, as required by EPA Method 1, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.
- 3.5.6.6.7 During the test run, make periodic adjustments to keep the temperature around the probe at the proper levels. Add more ice and, if necessary, salt, to maintain a temperature of <20°C (68°F) at the silica gel outlet. Also, periodically check the level and zero of the manometer.
- 3.5.6.6.8 A single train shall be used for the entire sampling run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. An additional train or additional trains may also be used for sampling when the capacity of a single train is exceeded.
- 3.5.6.6.9 When two or more trains are used, separate analyses of components from each train shall be performed. If multiple trains have been used because the capacity of a single train would be exceeded, first impingers from each train may be combined, and second impingers from each train may be combined.

- 3.5.6.6.10 At the end of the sampling run, turn off the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak check.

  Also, leak check the pitot lines as described in EPA Method 2. The lines must pass this leak check in order to validate the velocity-head data.
- 3.5.6.6.11 Calculate percent isokineticity (see Method 2) to determine whether the run was valid or another test should be made.

## 3.5.7 Sample Recovery

## 3.5.7.1 Preparation:

- 3.5.7.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling because a vacuum will be created, drawing liquid from the impingers back through the sampling train.
- 3.5.7.1.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet, being careful not to lose any condensate that might be present. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used, let any condensed water or liquid drain into the impingers. Cap off any open impinger inlets and outlets. Ground glass stoppers, Teflon caps or caps of other inert materials may be used to seal all openings.
- 3.5.7.1.3 Transfer the probe and impinger assembly to an area that is clean and protected from wind so that the chances of contaminating or losing the sample are minimized.
- 3.5.7.1.4 Inspect the train before and during disassembly, and note any abnormal conditions.

3.5.7.1.5 Save a portion of all washing solution (methylene chloride, water) used for cleanup as a blank. Transfer 200 ml of each solution directly from the wash bottle being used and place each in a separate, prelabeled sample container.

## 3.5.7.2 Sample Containers:

- 3.5.7.2.1 Container 1: Probe and Impinger Catches. Using a graduated cylinder, measure to the nearest ml, and record the volume of the solution in the first three impingers. Alternatively, the solution may be weighed to the nearest 0.5 g. Include any condensate in the probe in this determination. Transfer the impinger solution from the graduated cylinder into the amber flint glass bottle. Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all surfaces to which the sample is exposed (including the probe nozzle, probe fitting, probe liner, first impinger, and impinger connector) with methylene chloride. Use less than 500 ml for the entire wash (250 ml would be better, if possible). Add the washing to the sample container.
- 3.5.7.2.1.1 Carefully remove the probe nozzle and rinse the inside surface with methylene chloride from a wash bottle. Brush with a Teflon bristle brush, and rinse until the rinse shows no visible particles or yellow color, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with methylene chloride in a similar way.
- 3.5.7.2.1.2 Rinse the probe liner with methylene chloride. While squirting the methylene chloride into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with methylene chloride. Let the methylene chloride drain from the lower end into the sample container. The tester may use a funnel (glass or polyethylene) to aid in transferring the liquid washes to the container. Follow the rinse with a Teflon brush. Hold the probe in an inclined position, and squirt methylene chloride into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end

of the probe, and catch any methylene chloride, water, and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since there may be small crevices in which particulate matter can be entrapped. Rinse the brush with methylene chloride or water, and quantitatively collect these washing in the sample container. After the brushing, make a final rinse of the probe as described above.

NOTE: Two people should clean the probe in order to minimize sample losses. Between sampling runs, brushes must be kept clean and free from contamination.

- 3.5.7.2.1.3 Rinse the inside surface of each of the first three impingers (and connecting tubing) three separate times. Use a small portion of methylene chloride for each rinse, and brush each surface to which the sample is exposed with a Teflon bristle brush to ensure recovery of fine particulate matter. Water will be required for the recovery of the impingers in addition to the specified quantity of methylene chloride. There will be at least two phases in the impingers. This two-phase mixture does not pour well, and a significant amount of the impinger catch will be left on the walls. The use of water as a rinse makes the recovery quantitative. Make a final rinse of each surface and of the brush, using both methylene chloride and water.
- 3.5.7.2.1.4 After all methylene chloride and water washing and particulate matter have been collected in the sample container, tighten the lid so the solvent, water, and DNPH reagent will not leak out when the container is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Seal the container with Teflon tape. Label the container clearly to identify its contents.
- 3.5.7.2.1.5 If the first two impingers are to be analyzed separately to check for breakthrough, separate the contents and rinses of the two impingers into individual containers. Care must be taken to avoid physical carryover from the first impinger to the second. The formaldehyde

hydrazone is a solid which floats and froths on top of the impinger solution. Any physical carryover of collected moisture into the second impinger will invalidate a breakthrough assessment.

- 3.5.7.2.2 Container 2: Sample Blank. Prepare a blank by using an amber flint glass container and adding a volume of DNPH reagent and methylene chloride equal to the total volume in Container 1. Process the blank in the same manner as Container 1.
- 3.5.7.2.3 Container 3: Silica Gel. Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. The impinger containing the silica gel may be used as a sample transport container with both ends sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon caps maybe used. The silica gel impinger should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If the silica gel is removed from the impinger, the tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or other liquids to transfer the silica gel. If a balance is available in the field, the spent silica gel (or silica gel plus impinger) maybe weighed to the nearest 0.5 g.
- 3.5.7.2.4 Sample containers should be placed in a cooler, cooled by (although not in contact with) ice. Sample containers must be placed vertically and, since they are glass, protected from breakage during shipment. Samples should be cooled during shipment so they will be received cold at the laboratory.

# 3.5.8 Calibration

- 3.5.8.1 Probe Nozzle: Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in). when the nozzles become nicked or corroded, they shall be replaced and calibrated before use. Each nozzle must be permanently and uniquely identified.
- 3.5.8.2 Pitot Tube: The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2, or assigned a nominal coefficient of 0.84 if it is not visibly nicked or corroded and if it meets design and intercomponent spacing specifications.

### 3.5.8.3 Metering System

- 3.5.8.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak check be conducted. For metering systems having diaphragm pumps, the normal leak check procedure will not detect leakages with the pump. For these cases, the following leak check procedure will apply: make a ten-minute calibration run at 0.00057 m³/min (0.02 cfm). At the end of the run, take the difference of the measured wettest and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m³/min (0.02 cfm).
- 3.5.8.3.2 After each field use, check the calibration of the metering system by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). Set the vacuum at the maximum value reached during the test series. To adjust the vacuum, insert a

valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more the 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

3.5.8.3.3 Leak check of metering system: The portion of the sampling train from the pump to the orifice meter (see Figure 1) should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the following procedure: Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 - 18 cm (5 - 7 in) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks must be corrected.

NOTE: If the dry-gas-meter coefficient values obtained before and after a test series differ by >5%, either the test series must be voided or calculations for test series must be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

- 3.5.8.4 Probe Heater: The probe heating system must be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.
- 3.5.8.5 Temperature gauges: Each thermocouple must be permanently and uniquely marked on the casting. All mercury-in-glass reference thermometers must conform to ASTM E-1 63C or 63F specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at the ambient air temperatures, with and without the extension lead, must be noted

and recorded. Correction is necessary if the use of an extension lead produces a change >1.5%.

- 3.5.8.5.1 Impinger and dry-gas meter thermocouples: For the thermocouples used to measure the temperature of the gas leaving the impinger train, three-point calibration at ice water, room air, and boiling water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to  $\pm 2C$  (3.6°F) with those of the absolute value of the reference thermometer.
- 3.5.8.5.2 Probe and stack thermocouple: for the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice water, boiling water, and hot oil bath temperatures must be performed. Use of a point at room air temperature is recommended. The thermometer and thermocouple must agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.
- 3.5.8.6 Barometer: Adjust the barometer initially and before each test series to agree to within  $\pm 2.5$  mm Hg (0.1 in Hg) of the mercury barometer or the correct barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).
- 3.5.8.7 Triple-beam balance: Calibrate the triple-beam balance before each test series, using Class S standard weights. The weights must be within  $\pm 0.5$ % of the standards, or the balance must be adjusted to meet these limits.

# 3.5.9 <u>Calculations</u>

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

3.5.9.1 Calculation of Total Formaldehyde: To determine the total formaldehyde in mg, use the following equation:

Total mg formaldehyde -  $C_d \times V \times DF \times \frac{[g/\text{mole aldehyde}]}{[g/\text{mole DNPH derivative}]} \times 10^3 \text{ mg/}\mu\text{g}$ 

where:

 $C_{\rm d}$  = measured concentration of DNPH - formaldehyde derivative,  $\mu \rm g/ml$  V = organic extract volume ml

DF - dilution factor

3.5.9.2 Formaldehyde concentration in stack gas:

Determine the formaldehyde concentration in the stack gas using the following equation:

 $C_{f'}$  = K [total formaldehyde, mg]  $V_{m(std)}$  where:

K = 35.31 ft<sup>3</sup>/m<sup>3</sup> if  $V_{m(std)}$  is expressed in English units = 1.00 m<sup>3</sup>/m<sup>3</sup> if  $V_{m(std)}$  is expressed in metric units  $V_{m(std)}$  = volume of gas sample a measured by dry gas meter, corrected to standard conditions, dscm (dscf)

- 3.5.9.3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop are obtained from the data sheet.
- 3.5.9.4 Dry Gas Volume: Calculate  $V_{m(std)}$  and adjust for leakage, if necessary, using the equation in Section 6.3 of EPA Method 5.
- 3.5.9.5 Volume of Water Vapor and Moisture Content: Calculate the volume of water vapor and moisture content from equations 5-2 and 5-3 of EPA Method 5.

### 3.5.10 Determination of Volume to be Sampled

To determine the minimum sample volume to be collected, use the following sequence of equations.

3.5.10.1 From prior analysis of the waste feed, the concentration of formaldehyde (FORM) introduced into the combustion system can be calculated. The degree of destruction and removal efficiency that is required is used to determine the amount of FORM allowed to be present in the effluent. This amount may be expressed as:

Max FORM Mass = [ (WF) (FORM conc) (100 - %DRE) ] /100 where:

WF - mass flow rate of waste feed per h, g/h (lb/h)

FORM - concentration of FORM (wt %) introduced into the combustion process

DRE - percent Destruction and Removal Efficiency required

3.5.10.2 The average discharge concentration of the FORM in the effluent gas is determined by comparing the Max FORM with the volumetric flow rate being exhausted from the source. Volumetric flow rate data are available as a result of preliminary EPA Method 1 - 4 determinations:

Max FORM conc = [Max FORM Mass] /  $DV_{eff(std)}$  where:

3.5.10.3 In making this calculation, it is recommended that a safety margin of at least ten be included.

[LDL<sub>FORM</sub> x 10 / FORM conc] =  $V_{tbc}$ 

where:

 ${
m LDL_{FORM}}$  - detectable amount of FORM in entire sampling train  ${
m V_{tbc}}$  - minimum dry standard volume to be collected at drygas meter

3.5.10.4 The following analytical detection limits and DNPH Reagent Capacity (based on a total volume of 200 ml in two impingers) must also be considered in determining a volume to be sampled.

#### 3.5.11 Quality Control

- 3.5.11.1 Sampling: See EPA Manual 600/4-77-02b for Method 5 quality control.
- 3.5.11.2 Analysis: The quality assurance program required for this method includes the analysis of the field and method blanks, procedure validations, and analysis of field spikes. The assessment of combustion data and positive identification and quantitation of formaldehyde are dependent on the integrity of the samples received and the precision and accuracy of the analytical methodology. Quality assurance procedures for this method are designed to monitor the performance of the analytical methodology and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.
- 3.5.11.2.1 Field Blanks: Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, methylene chloride and water, and unused DNPH reagent. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling are, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual sampling train). The probe of the blank train must be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the blank sampling train.
- 3.5.11.2.2 Method Blanks: A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

3.5.11.2.3 Field Spike: A field spike is performed by introducing 200  $\mu$ L of the Field Spike Standard into an impinger containing 200 ml of DNPH solution. Standard impinger recovery procedures are followed and the spike is used as a check on field handling and recovery procedures. An aliquot of the field spike standard is retained in the laboratory for derivatization and comparative analysis.

#### 3.5.12 <u>Method Performance</u>

3.5.12.1 Method performance evaluation: The expected method performance parameters for precision, accuracy, and detection limits are provided in Table 3.5-3.

Addition of a Filter to the Formaldehyde Sampling Train

As a check on the survival of particulate material through the impinger system, a filter can be added to the impinger train either after the second impinger or after the third impinger. Since the impingers are in an ice bath, there is no reason to heat the filter at this point.

Any suitable medium (e.g., paper, organic membrane) may be used for the filter if the material conforms to the following specifications:

- the filter has at least 95% collection efficiency (<5% penetration) for 3  $\mu$ m dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose.
- the filter has a low aldehyde blank value (<0.015 mg formaldehyde/cm² of filter area). Before the test series, determine the average formaldehyde blank value of at least three filters (from the lot to be used for sampling) using the applicable analytical procedures.

# EXPECTED METHOD PERFORMANCE FOR FORMALDEHYDE

Parameter		Precision <sup>1</sup>	Accuracy <sup>2</sup>	Detection Limit <sup>3</sup>	
Matrix:	Dual trains	±15% RPD	<u>+</u> 20%	1.5 x 10 <sup>-7</sup> 1b/ft <sup>3</sup>	
				(1.8 ppbv)	

<sup>&</sup>lt;sup>1</sup>Relative percent difference limit for dual trains.

<sup>&</sup>lt;sup>2</sup>Limit for field spike recoveries.

<sup>&</sup>lt;sup>3</sup>The lower reporting limit having less than 1% probability of false positive detection.

Recover the exposed filter into a separate clean container and return the container over ice to the laboratory for analysis. If the filter is being analyzed for formaldehyde, the filter may be recovered into a container or DNPH reagent for shipment back to the laboratory. If the filter is being examined for the presence of particulate material, the filter may be recovered into a clean dry container and returned to the laboratory.

# 3.6 Analysis for Aldehydes and Ketones by High Performance Liquid Chromatography (HPLC) (Method 0011A)

#### 3.6.1 Scope and Application

3.6.1.1 Method 0011A covers the determination of free formaldehyde in the aqueous samples and leachates and derived aldehydes/ketones collected by Method 0011.

Compound Name	CAS No.*
Formaldehyde	50-00-0
Acetaldehyde	75-07-0

- \* Chemical Abstract Services Registry Number
- 3.6.1.2 Method 0011A is a high performance liquid chromatographic (HPLC) method optimized for the determination of formaldehyde and acetaldehyde in aqueous environmental matrices and leachates of solid samples and stack samples collected by Method 0011. When this method is used to analyze unfamiliar sample matrices, compound identification should be supported by at least one additional qualitative technique. A gas chromatograph/mass spectrometer (GC/MS) may be used for the qualitative confirmation of results from the target analytes, using the extract produced by this method.
- 3.6.1.3 The method detection limits (MDL) are listed in Tables 3.6-1 and 3.6-2. The MDL for a specific sample may differ from that listed, depending upon the nature of interferences in the sample matrix and the amount of sample used in the procedure.
- 3.6.1.4 The extraction procedure for solid samples is similar to that specified in Method 1311 (1). Thus, a single sample may be extracted to measure the analytes included in the scope of other appropriate methods. The analyst is allowed the flexibility to select chromatographic conditions

Table 3.6-1

# HIGH PERFORMANCE LIQUID CHROMATOGRAPHY CONDITIONS AND METHOD DETECTION LIMITS USING SOLID SORBENT EXTRACTION

Analyte	Retention Time (minutes)	MDL (µg/L)*
Formaldehyde	7.1	7.2

HPLC conditions: Reverse phase C18 column, 4.6 x 250 mm; isocratic elution using methanol/water (75:25, v/v); flow rate 1.0 mL/min.; detector 360 nm.

Table 3.6-2

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY CONDITIONS
AND METHOD DETECTION LIMITS USING METHYLENE
CHLORIDE EXTRACTION

Analyte	Retention Time (minutes)	MDL (μg/L)*
Formaldehyde	7.1	7.2
Acetaldehyde	8.6	171*

HPLC conditions: Reverse phase C18 column, 4.6 x 250 mm; isocratic elution using methanol/water (75:25, v/v); flow rate 1.0 mL/min.; detector 360 nm.

<sup>\*</sup> After correction for laboratory blank.

<sup>\*</sup> These values include reagent blank concentrations of approximately 13  $\mu g/L$  formaldehyde and 130  $\mu g/L$  acetaldehyde.

appropriate for the simultaneous measurement of contaminations of these analytes.

- 3.6.1.5 This method is restricted to use by, or under the supervision of analysts experienced in the use of chromatography and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.
- 3.6.1.6 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.
- 3.6.1.7 Formaldehyde has been tentatively classified as a known or suspected, human or mammalian carcinogen.

# 3.6.2 <u>Summary of Method</u>

### 3.6.2.1 Environmental Liquids and Solid Leachates

3.6.2.1.1 For wastes comprised of solids or for aqueous wastes containing significant amounts of solid material, the aqueous phase, if any, is separated from the solid phase and stored for later analysis. If necessary, the particle size of the solids in the waste is reduced. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase of the waste. A special extractor vessel is used when testing for volatiles. Following extraction, the aqueous extract is separated from the solid phase by filtration employing 0.6 to 0.8  $\mu$ m glass fiber filters.

- 3.6.2.1.2 If compatible (i.e., multiple phases will not form on combination), the initial aqueous phase of the waste is added to the aqueous extract, and these liquids are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume weighted average concentration.
- 3.6.2.1.3 A measured volume of aqueous sample or an appropriate amount of solids leachate is buffered to pH 5 and derivatized with 2,4-dinitrophenylhydrazine (DNPH), using either the solid sorbent or the methylene derivatization/extraction option. If the solid sorbent option is used, the derivative is extracted using solid sorbent cartridges, followed by elution with ethanol. If the methylene chloride option is used, the derivative is extracted with methylene chloride. The methylene chloride extracts are concentrated using the Kuderna-Danish (K-D) procedure and solvent exchanged into methanol prior to HPLC analysis. Liquid chromatographic conditions are described which permit the separation and measurement of formaldehyde in the extract by absorbance detection at 360 nm.

### 3.6.2.2 Stack Gas Samples Collected by Method 0011

- 3.6.2.2.1 The entire sample returned to the laboratory is extracted with methylene chloride and the methylene chloride extract is brought up to a known volume. An aliquot of the methylene chloride extract is solvent exchanged and concentrated or diluted as necessary.
- 3.6.2.2.2 Liquid chromatographic conditions are described that permit the separation and measurement of formaldehyde in the extract by absorbance detection at 360 nm.

# 3.6.3 <u>Interferences</u>

3.6.3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of

these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks.

- 3.6.3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and distilled water. It should then be drained, dried, and heated in a laboratory oven at 130°C for several hours before use. Solvent rinses with methanol may be substituted for the oven heating. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.
- 3.6.3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.
- 3.6.3.2 Analysis for formaldehyde is especially complicated by its ubiquitous occurrence in the environment.
- 3.6.3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. No interferences have been observed in the matrices studied as a result of using solid sorbent extraction as opposed to liquid extraction. If interferences occur in subsequent samples, some additional cleanup may be necessary.
- 3.6.3.4 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the HPLC conditions described allow for a resolution of the specific compounds covered by this method, other matrix components may interfere.

#### 3.6.4 Apparatus and Materials

3.6.4.1 Reaction vessel - 250 ml Florence flask.

- 3.6.4.2 Separatory funnel 205 ml, with Teflon stopcock
  - 3.6.4.3 Kuderna-Danish (K-D) apparatus.
- 3.6.4.3.1 Concentrator tube 10 ml graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.
- 3.6.4.3.2 Evaporation flask 500 ml (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.
- 3.6.4.3.3 Snyder column Three ball macro (Kontes K-503000-0121 or equivalent).
- 3.6.4.3.4 Snyder column Two ball macro (Kontes K-569001-0219 or equivalent).
  - 3.6.4.3.5 Springs 1/2 inch (Kontes K-662750 or equivalent).
- 3.6.4.4 Vials 10, 25 ml, glass with Teflon lined screw caps or crimp tops.
- 3.6.4.5 Boiling chips Solvent extracted with methylene chloride, approximately 10/40 mesh (silicon carbide or equivalent).
- 3.6.4.6 Balance Analytical, capable of accurately weighing to the nearest 0.0001 g.
  - 3.6.4.7 pH meter Capable of measuring to the nearest 0.01 units.
  - 3.6.4.8 High performance liquid chromatograph (modular)
- 3.6.4.8.1 Pumping system Isocratic, with constant flow control capable of 1.00 ml/min.
  - 3.6.4.8.2 High pressure injection valve with 20  $\mu$ L loop.
- 3.6.4.8.3 Column 250 mm x 4.6 mm ID, 5  $\mu$ m particle size, C18 (or equivalent).
  - 3.6.4.8.4 Absorbance detector 360 nm.

- 3.6.4.8.5 Strip-chart recorder compatible with detector Use of a data system for measuring peak areas and retention times is recommended.
  - 3.6.4.9 Glass fiber filter paper.
- 3.6.4.10 Solid sorbent cartridges Packed with 500 mg C18 (Baker or equivalent).
- 3.6.4.11 Vacuum manifold Capable of simultaneous extraction of up to 12 samples (Supelco or equivalent).
- 3.6.4.12 Sample reservoirs 60 ml capacity (Supelco or equivalent).
- 3.6.4.13 Pipet Capable of accurately delivering 0.10 ml solution (Pipetman or equivalent).
- 3.6.4.14 Water bath Heated, with concentric ring cover, capable of temperature control ( $(\pm)$  2°C). The bath should be used under a hood.
  - 3.6.4.15 Volumetric Flasks 250 or 500 ml.

# 3.6.5 Reagents

- 3.6.5.1 Reagent grade chemicals shall be used in all tests.
  Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.
- 3.6.5.2 Organic-free water All references to water in this method refer to organic-free reagent water, as defined in Chapter I SW-846.

- 3.6.5.3 Methylene chloride, CH<sub>2</sub>Cl<sub>2</sub> HPLC grade or equivalent.
  - 3.6.5.4 Methanol, CH<sub>3</sub>OH HPLC grade or equivalent.
  - 3.6.5.5 Ethanol (absolute), CH<sub>3</sub>CH<sub>2</sub>OH HPLC grade or equivalent.
- 3.6.5.6 2,4-Dinitrophenylhydrazine (DNPH) (70% (W/W)), [2,4- $(O_2N)_2C_6H_3$ ] NHNH<sub>2</sub>, in organic-free reagent water.
- 3.6.5.7 Formalin (37.6 percent (w/w)), formaldehyde in organic-free reagent water.
  - 3.6.5.8 Acetic acid (glacial), CH<sub>3</sub>CO<sub>2</sub>H.
  - 3.6.5.9 Sodium hydroxide solutions NaOH, 1.0 N and 5 N.
  - 3.6.5.10 Sodium chloride, NaCl.
  - 3.6.5.11 Sodium sulfite solution, Na<sub>2</sub>SO<sub>3</sub>, 0.1 M.
  - 3.6.5.12 Hydrochloric Acid, HCl, 0.1 N.
- 3.6.5.13 Extraction fluid Dilute 64.3 ml of 1.0 N NaOH and 5.7 ml glacial acetic acid to 900 ml with organic-free reagent water. Dilute to 1 liter with organic-free reagent water. The pH should be  $4.93 \pm 0.02$ .
  - 3.6.5.14 Stock standard solutions
- 3.6.5.14.1 Stock formaldehyde (approximately 1.00 mg/ml) Prepare by diluting 265  $\mu$ l formalin to 100 ml with organic-free reagent water.
- 3.6.5.14.1.1 Standardization of formaldehyde stock solution Transfer a 25 ml aliquot of a 0.1 M Na<sub>2</sub>SO<sub>3</sub> solution to a beaker and record the pH. Add a 25.0 ml aliquot of the formaldehyde stock solution (Section 3.6.5.14.1) and record the pH. Titrate this mixture back to the original pH

using 0.1 N HCl. The formaldehyde concentration is calculated using the following equation:

Concentration (mg/ml) =  $30.03 \times (N \text{ HCl}) \times (m1 \text{ HCl}) 25.0$ 

N HCl - Normality of HCl solution used ml HCl - ml of standardized HCl solution used 30.03 - MW of formaldehyde

- 3.6.5.14.2 Stock formaldehyde and acetaldehyde Prepare by adding 265  $\mu$ L formalin and 0.1 g acetaldehyde to 90 ml of water and dilute to 100 ml. The concentration of acetaldehyde in this solution is 1.00 mg/ml. Calculate the concentration of formaldehyde in this solution using the results of the assay performed in Section 3.6.5.14.1.1.
- 3.6.5.14.3 Stock standard solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

### 3.6.5.15 Reaction Solutions

- 3.6.5.15.1 DNPH (1.00  $\mu$ g/L) Dissolve 142.9 mg of 70% (w/w) reagent in 100 ml absolute ethanol. Slight heating or sonication may be necessary to effect dissolution.
- 3.6.5.15.2 Acetate buffer (5 N) Prepare by neutralizing glacial acetic acid to pH 5 with 5 N NaOH solution. Dilute to standard volume with water.
- 3.6.5.15.3 Sodium chloride solution (saturated) Prepare by mixing of the reagent grade solid with water.

# 3.6.6 Sample Collection. Preservation, and Handling

3.6.6.1 See the introductory material to this Chapter, Organic Analytes, Section 4.1 of SW-846.

- 3.6.6.2 Environmental liquid and leachate samples must be refrigerated at 4°C, and must be derivatized within 5 days of sample collection and analyzed within 3 days of derivatization.
- 3.6.6.3 Stack gas samples collected by Method 0011 must be refrigerated at 4°C. It is recommended that samples be extracted within 30 days of collection and that extracts be analyzed within 30 days extraction.

### 3.6.7 Procedure

- 3.6.7.1 Extraction of Solid Samples
- 3.6.7.1.1 All solid samples should be homogeneous. When the sample is not dry, determine the dry weight of the sample, using a representative aliquot.
- 3.6.7.1.1.1 Determination of dry weight In certain cases, sample results are desired based on a dry weight basis. When such data is desired, or required, a portion of sample for dry weight determination should be weighed out at the same time as the portion used for analytical determination.
- WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample.
- 3.6.7.1.1.2 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:
  - \$ dry weight = g of dry sample x 100
    g of sample
- 3.6.7.1.2 Measure 25 g of solid into a 500 ml bottle with a Teflon lined screw cap or crimp top, and add 500 ml of extraction fluid (Section 3.6.5.13). Extract the solid by rotating the bottle at approximately 30 rpm

for 18 hours. Filter the extract through glass fiber paper and store in sealed bottles at 4°C. Each ml of extract represents 0.050 g solid.

#### 3.6.7.2 Cleanup and Separation

- 3.6.7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of various sample types. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of formaldehyde is no less then 85% of recoveries specified in Table 3.6-3. Recovery may be lower for samples which form emulsions.
- 3.6.7.2.2 If the sample is not clean, or the complexity is unknown, the entire sample should be centrifuged at 2500 rpm for 10 minutes. Decant the supernatant liquid from the centrifuge bottle, and filter through glass fiber filter paper into a container which can be tightly sealed.

# 3.6.7.3 Derivatization

- 3.6.7.3.1 For aqueous samples, measure a 50 to 100 ml aliquot of the sample. Quantitatively transfer the sample aliquot to the reaction vessel (Section 3.6.4.1).
- 3.6.7.3.2 For solid samples, 1 to 10 ml of leachate (Section 3.6.7.1) will usually be required. The amount used for a particular sample must be determined through preliminary experiments.

Table 3.6-3

# SINGLE OPERATOR ACCURACY AND PRECISION USING SOLID SORBENT EXTRACTION

Analyte	Matrix Type	Average Percent Recovery	Standard Deviation Percent	Spike Range (µg/L)	Number of Analyses
Formaldehyde	Reagent Water	86	9.4	15-1430	39
	Final Effluent	90	11.0	46.8-1430	16
	Phenol formaldehyde Sludge	93	12.0	457-1430	15

Note: For all reactions, the total volume of the aqueous layer should be adjusted to 100 ml with water.

3.6.7.3.3 Derivatization and extraction of the derivative can be accomplished using the solid sorbent (Section 3.6.7.3.4) or methylene chloride option (Section 3.6.7.3.5).

# 3.6.7.3.4 Solid Sorbent Option

- 3.6.7.3.4.1 Add 4 ml of acetate buffer and adjust the pH to 5.0  $\pm$  0.1 with glacial acetic acid or 5 N NaOH. Add 6 ml of DNPH reagent, seal the container, and place on a wrist-action shaker for 30 minutes.
- 3.6.7.3.4.2 Assemble the vacuum manifold and connect to a water aspirator or vacuum pump. Assemble solid sorbent cartridges containing a minimum of 1.5 g of Cl8 sorbent, using connectors supplied by the manufacturer, and attach the sorbent train to the vacuum manifold. Condition each cartridge by passing 10 ml dilute acetate buffer (10 ml 5 N acetate buffer dissolved in 250 ml water) through the sorbent cartridge train.
- 3.6.7.3.4.3 Remove the reaction vessel from the shaker and add 10 ml saturated NaCl solution to the vessel.
- 3.6.7.3.4.4 Add the reaction solution to the sorbent train and apply a vacuum so that the solution is drawn through the cartridges at a rate of 3 to 5 ml/min. Release the vacuum after the solution has passed through the sorbent.
- 3.6.7.3.4.5 Elute each cartridge train with approximately 9 ml of absolute ethanol, directly into a 10 ml volumetric flask. Dilute the solution to volume with absolute ethanol, mixed thoroughly, and place in a tightly sealed vial until analyzed.

# 3.6.7.3.5 Methylene Chloride Option

- 3.6.7.3.5.1 Add 5 m of acetate buffer and adjust the pH to  $5.0\pm0.5$  with glacial acetic acid or 5 N NaOH. Add 10 ml of DNPH reagent, seal the container, and place on a wrist-action shaker for 1 hour.
- 3.6.7.3.5.2 Extract the solution with three 20 ml portions of methylene chloride, using a 250 ml separatory funnel, and combine the methylene chloride layers. If an emulsion forms upon extraction, remove the entire emulsion and centrifuge at 2000 rpm for 10 minutes. Separate the layers and proceed with the next extraction.
- 3.6.7.3.5.3 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 ml concentrator tube to a 500 ml evaporator flask. Wash the K-D apparatus with 25 ml of extraction solvent to complete the quantitative transfer.
- 3.6.7.3.5.4 Add one to two clean boiling chips to the evaporative flask and attach a three ball Snyder column. Preset the Snyder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 10 ml, remove the K-D apparatus and allow it to drain and cool for a least 10 min.
- 3.6.7.3.5.5 Prior to liquid chromatographic analysis, the solvent must be exchanged to methanol. The analyst must ensure quantitative transfer of the extract concentrate. The exchange is performed as follows:

- 3.6.7.3.5.5.1 Following K-D concentration of the methylene chloride extract to < 10 ml using the macro Snyder column, allow the apparatus to cool and drain for at least 10 minutes.
- 3.6.7.3.5.5.2 Momentarily remove the Snyder column, add 5 ml of the methanol, a new glass bed, or boiling chip, and attach the micro Snyder column. Concentrate the extract using 1 ml of methanol to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches < 5 ml, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.
- 3.6.7.3.5.5.3 Remove the Snyder column and rinse the flask and its lower joint with 1-2 ml of methanol and add to concentrator tube. A 5-ml syringe is recommended for this operation. Adjust the extract volume to 10 ml. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon-lined screw cap or crimp top. Proceed with liquid chromatographic analysis if further cleanup is not required.
  - 3.6.7.4 Extraction of Stack Gas Samples Collected by Method 0011
- 3.6.7.4.1 Measure the aqueous volume of the sample prior to extraction (for moisture determination in case the volume was not measured in the field). Pour the sample into a separatory furmel and drain the methylene chloride into a volumetric flask.
- 3.6.7.4.2 Extract the aqueous solution with two or three aliquots of methylene chloride. Add the methylene chloride extracts to the volumetric flask.

- 3.6.7.4.3 Fill the volumetric flask to the line with methylene chloride. Mix well and remove an aliquot.
- 3.6.7.4.4 If high levels of formaldehyde are present, the extract can be diluted with mobile phase, otherwise the extract must be solvent exchanged as described in Section 3.6.7.5.3.3. If low levels of formaldehyde are present, the sample should be concentrated during the solvent exchange procedure.

### 3.6.7.5 Chromatographic Conditions

Column: C18, 250 mm x 4.6 mm ID, 5  $\mu$ m particle size

Mobile Phase: methanol/water, 75:25 (v/v), isocratic

Flow Rate: 1.0 ml/min

UV Detector: 360 nm Injection Volume: 20  $\mu$ l

### 3.6.7.6 Calibration

3.6.7.6.1 Establish liquid chromatographic operating parameters to produce a retention time equivalent to that indicated in Table 3.6-1 for the solid sorbent options, or in Table 3.6-2 for methylene chloride option.

Suggested chromatographic conditions are provided in Section 3.6.7.5. Prepare derivatized calibration standards according to the procedure in Section 3.6.7.6.1.1. Calibrate the chromatographic system using the external standard technique (Section 3.6.7.6.1.2).

### 3.6.7.6.1.1 Preparation of calibration standards

3.6.7.6.1.1.1 Prepare calibration standard solutions of formaldehyde and acetaldehyde in water from the stock standard (Section 3.6.5.14.2). Prepare these solutions at the following concentrations (in  $\mu g/ml$ ) by serial dilution of the stock standard solution: 50, 20, 10. Prepare additional calibration standard solutions at the following concentrations, by dilution of the appropriate 50, 20, or 10  $\mu g/ml$  standard: 5, 0.5, 2, 0.2, 1, 0.1.

3.6.7.6.1.1.2 Process each calibration standard solution through the derivatization option used for sample processing (Section 3.6.7.3.4 or 3.6.7.3.5).

#### 3.6.7.6.1.2 External standard calibration procedure

- 3.6.7.6.1.2.1 Analyze each derivatized calibration standard using the chromatographic conditions listed in Tables 3.6-1 and 3.6-2, and tabulate peak area against concentration injected. The results may be used to prepare calibration curves for formaldehyde and acetaldehyde.
- 3.6.7.6.1.2.2 The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the previously established responses by more the 10%, the test must be repeated using a fresh calibration standard after it is verified that the analytical system is in control. Alternatively, a new calibration curve may be prepared for that compound. If an autosampler is available, it is convenient to prepare a calibration curve daily by analyzing standards along with test samples.

# 3.6.7.7 Analysis

- 3.6.7.7.1 Analyze samples by HPLC, using conditions established in Section 3.6.7.6.1. Tables 3.6-1 and 3.6-2 list the retention times and MDLs that were obtained under these conditions. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements for Section 3.6.8.1 are met, or if the data are within the limits described in Tables 3.6-1 and 3.6-2.
- 3.6.7.7.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatograms.

- 3.6.7.7.3 If the peak area exceeds the linear range of the calibration curve, a smaller sample volume should be used. Alternatively, the final solution may be diluted with ethanol and reanalyzed.
- 3.6.7.7.4 If the peak area measurement is prevented by the presence of observed interferences, further cleanup is required. However, none of the 3600 method series have been evaluated for this procedure.

# 3.6.7.8 Calculations

3.6.7.8.1 Calculate each response factor as follows (mean value based on 5 points):

RF - concentration of standard area of the signal

mean = RF = 
$$\overline{RF}$$
 =  $\frac{(\sum_{i=1}^{5} RF_{i})}{5}$ 

3.6.7.8.2 Calculate the concentration of formaldehyde and acetaldehyde as follows:

 $\mu$ g/ml = (RF) (area of signal) (concentration factor)

where:

NOTE: For solid samples, a dilution factor must be included in the equation to account for the weight of the sample used.

3.6.7.8.3 Calculate the total weight of formaldehyde in the stack gas sample as follows:

total  $\mu g/ml = (RF)$  (area of signal) (concentration factor)

where:

concentration factor = 

Initial Extract Volume

### 3.6.8 Quality Control

3.6.8.1 Refer to Chapter One of SW-846 for guidance on quality control procedures.

# 3.6.9 <u>Method Performance</u>

- 3.6.9.1 The MDL concentrations listed in Table 3.6-1 were obtained using organic-free water and solid sorbent extraction. Similar results were achieved using a final effluent and sludge leachate. The MDL concentrations listed in Table 3.6-2 were obtained using organic-free water and methylene chloride extraction. Similar results were achieved using representative matrices.
- 3.6.9.2 This method has been tested for linearity of recovery from spiked organic-free water and has been demonstrated to be applicable over the range from 2 x MDL to 200 x MDL.
- 3.6.9.3 In a single laboratory evaluation using several spiked matrices, the average recoveries presented in Tables 3.6-3 and 3.6-4 were obtained using solid sorbent and methylene chloride extraction, respectively. The standard deviations of the percent recovery are also included in Tables 3.6-3 and 3.6-4.
- 3.6.9.4 A representative chromatogram is presented in Figure 3.6-1.

# 3.6.10 References

- 1. Federal Register, 1986, 51, 40643-40652; November 7.
- 2. EPA Methods 6010, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C. 20460.

ALE ARERATAR ACCUMACY AND RESCICTAN

# SINGLE OPERATOR ACCURACY AND PRECISION USING METHYLENE CHLORIDE EXTRACTION

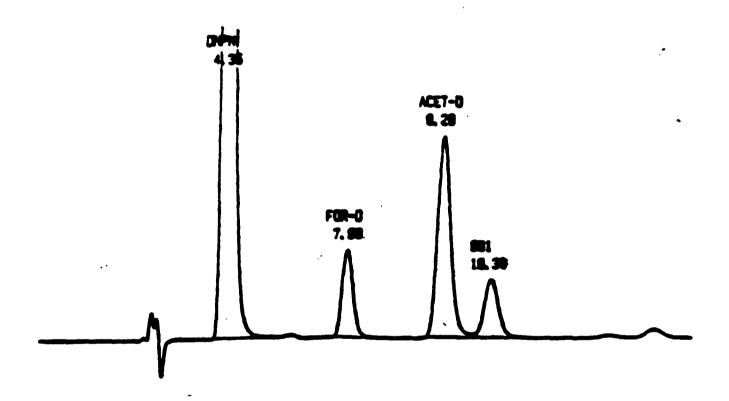
Table 3.6-4

Analyte	Matrix Type	Average Percent Recovery X	Standard Deviation Percent P	Spike Range (µg/L)	Number of Analyses
Formaldehyde	Reagent Wâter	91	2.5	50-1000	9
	Ground- water	92.5	8.2	50	6
	Liquids	69.6	16.3	250	12
Acetaldehyde	Resgent Water	60.3	3.2	50-1000	9
	Ground- water	63.6	10.9	50	12 .
	Liquids (2 types)	44.0	20.2	250	12
	Solids	58.4	2.7	0.10-1.0	12

Spike range in units of mg/g.

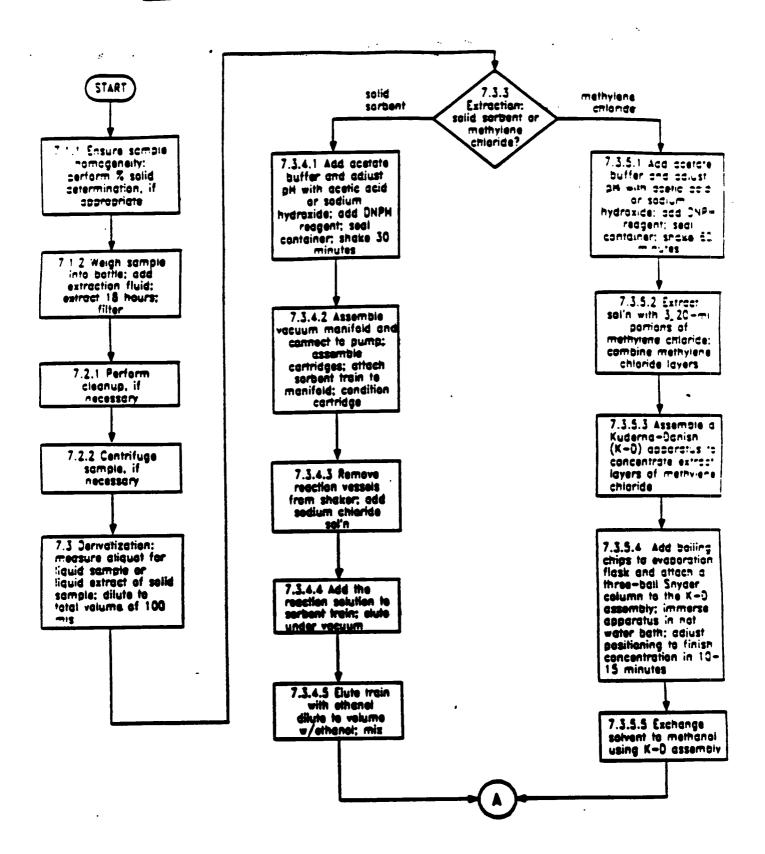
x - Average recovery expected for this method

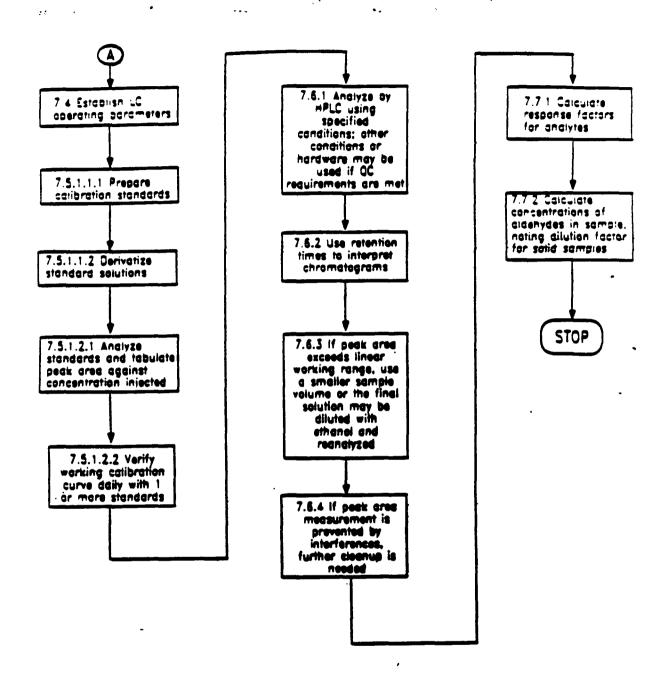
p - Average standard deviation expected for this method.



FOR-D = Formaldehyde derivative ACET-D = Acetaldehyde derivative

# METHOD 0011A FORMALDEHYDE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)





# Section 4.0.

# PROCEDURE FOR ESTIMATING THE TOXICITY EQUIVALENCY OF CHLORINATED DIBENZO-P-DIOXIN AND DIBENZOFURAN CONGENERS

PCDDs and PCDFs must be determined using the method given in Section 3.4 of this document. In this method, individual congeners or homologues are measured and then summed to yield a total PCDD/PCDF value. No toxicity factors are specified in the method to compute risks from such emissions.

For the purpose of estimating risks posed by emissions from boilers and industrial furnaces, however, specific congeners and homologues must be measured using the specified method and then multiplied by the assigned toxicity equivalence factors (TEFs), using procedures described in "Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs and CDFs) and 1989 Update," EPA/625/3-89/016, March 1989. The resulting 2,3,7,8-TCDD equivalents value is used in the subsequent risk calculations and modeling efforts as discussed in the BIF final rule.

The procedure for calculating the 2,3,7,8-TCDD equivalent is as follows:

- 1. Using Method 23, determine the concentrations of 2,7,3,8-congeners of various PCDDs and PCDFs in the sample.
- 2. Multiply the congener concentrations in the sample by the TEF listed in Table 4.0-1 to express the congener concentrations in terms of 2,3,7,8-TCDD equivalent. Note that congeners not

¹The term "congener" refers to any one particular member of the same chemical family; e.g., there are 75 congeners of chlorinated dibenzo-p-dioxins. The term "homologue" refers to a group of structurally related chemicals that have the same degree of chlorination. For example, there are eight homologues of CDs, monochlorinated through octachlorinated. Dibenzo-p-dioxins and dibenzofurans that are chlorinated at the 2,3,7, and 8 positions are denoted as "2378" congeners, except when 2,3,7,8-TCDD is uniquely referred to: e.g., 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF are both referred to as "2378-PeCDFs."

Table 4.0-1

2,3,7,8-TCDD TOXICITY EQUIVALENCE FACTORS (TEFs)<sup>1</sup>

Compound	I-TEFs, 89
Mono-, Di-, and TriCDDs	0
2,3,7,8-TCDD Other TCDDS	1 0
2,3,7,8-PeCDD Other PeCDDs	0.5
2,3,7,8-HxCDD Other HxCDDs	0.1
2,3,7,8-HpCDD Other HpCDDs	0.01 0
OCDD	0.001
Mono-, Di-, and TriCDFs	0
2,3,7,8-TCDF Other TCDFs	0.1
1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF Other PeCDFs	0.05 0.5 0
2378-HxCDFs Other HxCDFs	0.1
2378-HpCDFs Other HpCDFs	0.01 0
OCDF	0.001

Reference: Adapted from NATO/CCMS, 1988a.

<sup>&</sup>lt;sup>1</sup>Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs and CDFs) 1989 Update EPA/625/3-89/016, March 1989

chlorinated at 2,3,7 and 8 positions have a zero toxicity factor in this table.

3. Add the products obtained in step 2, to obtain the total 2,3,7,8-TCDD equivalent in the sample.

Sample calculations are provided in EPA document No. EPA/625/3-89/016, March 1989, which can be obtained from the EPA, ORD Publications Office, Cincinnati, Ohio (Phone no. 513-569-7562).

#### Section 5.0

## HAZARDOUS WASTE COMBUSTION AIR QUALITY SCREENING PROCEDURE

The HWCAQSP is a combined calculation/reference table approach for conservatively estimating short-term and annual average facility impacts for stack emissions. The procedure is based on extensive short-term modeling of 11 generic source types and on a set of adjustment factors for estimating annual average concentrations from short-term concentrations. Facility impacts may be determined based on the selected worst-case stack or on multiple stacks, in which the impacts from each stack are estimated separately and then added to produce the total facility impact.

This procedure is most useful for facilities with multiple stacks, large source-to-property boundary distances, and complex terrain between 1 and 5 km from the facility. To ensure a sufficient degree of conservatism, the HWCAQSP may not be used if any of the five screening procedure limitations listed below are true:

- The facility is located in a narrow valley less than 1 km wide;
- The facility has a stack taller than 20 m and is located such that the terrain rises to the stack height within 1 km of the facility;
- The facility has a stack taller then 20 m and is located within 5 km of the shoreline of a large body of water;
- The facility property line is within 200 m of the stack and the physical stack height is less than 10 m; or
- On-site receptors are of concern, and stack height is less than 10 m.

If any of these criteria are met or the Director determines that this procedure is not appropriate, then detailed site-specific modeling or modeling using the "Screening Procedures for Estimating the Air Quality Impact of Stationary Sources," EPA -450/4-88-010, Office of Air Quality Planning and

Standards, August 1988, is required. Detailed site-specific dispersion modeling must conform to the EPA "Guidance on Air Quality Models (Revised)", EPA 450/2-78-027R, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, July 1986. This document provides guidance on both the proper selection and regulatory application of air quality models.

#### Introduction

The Hazardous Waste Combustion Air Quality Screening Procedure (HWCAQSP) (also referred to hereafter as "the screening procedure" or "the procedure") provides a quick, easy method for estimating maximum (hourly) and annual average ambient air impacts associated with the combustion of hazardous waste. The methodology is conservative in nature and estimates dispersion coefficients based on facility-specific information.

The screening procedure can be used to determine emissions limits at sites where the nearest meteorological (STAR) station is not representative of the meteorology at the site. If the screen shows that emissions from the site are adequately protective, then the need to collect site-specific meteorological data can be eliminated.

The screening procedure is generally most helpful for facilities meeting one or more of the following conditions:

- Multiple stacks with substantially different release specifications (e.g., stack heights differ by >50 percent, exit temperatures differ by >50°K, or the exit follow rates differ by more than a factor of 2),
- Terrain located between 1 km and 5 km from the site increases in elevation by more than the physical height of the shortest stack (i.e., the facility is located in complex terrain), or

<sup>&</sup>lt;sup>1</sup>The term dispersion coefficient refers to the change in ambient air concentration  $(\mu g/m^3)$  resulting from a source with an emission rate of 1 g/sec.

 Significant distance between the facility's stacks and the site boundary [guidance on determining whether a distance is "significant" is provided in Step 6(B) of the procedure].

Steps 1 through 9 of the screening procedure present a simplified method for determining emissions based on the use of the "worst-case" stack. If the simplified method shows that desired feed rates result in emissions that exceed allowable limits for one or more pollutants, a refined analysis to examine the emissions from each stack can be conducted. This multiple-stack method is presented in Step 10.

The steps involved in screening methodology are as follows:

- Step 1. Define Source Characteristics
- Step 2. Determine the Applicability of the Screening Procedure
- Step 3. Select the Worst-Case Stack
- Step 4. Verify Good Engineering Practice (GEP) Criteria
- Step 5. Determine the Effective Stack Height and Terrain-Adjusted Effective Stack Height
- Step 6. Classify the Site as Urban or Rural
- Step 7. Determine Maximum Dispersion Coefficients
- Step 8. Estimate Maximum Ambient Air Concentrations
- Step 9. Determine Compliance with Regulatory Limits
- Step 10. Multiple Stack Method

## Step 1: Define Source Characteristics

Provide the following source data:2

<sup>&</sup>lt;sup>2</sup>Worksheet space is provided for three stacks. If the facility has additional stacks, copy the form and revise stack identification numbers for 4, 5, etc.

Stäck Data: Stack No. 1 . Stac	k No. 2 Stack No.	3
Physical stack height (m)	<del></del>	_
Exhaust temperature (*K)		_
Flow rate (m <sup>3</sup> /sec)		_
	,	
Nearby Building Dimensions:		
Consider all buildings within five building heigh	its or five maximum pr	ojected
widths of the stack(s). For the building with the	e greatest height, fi	.11 in
the spaces below.		
Building Height (m)		
Maximum projected building width (		
imalimum projectico burraring wracii (	<del>-</del> /	<del></del>
Nearby Terrain Data:		
Determine maximum terrain rise for the following	three distance ranges	from
the facility (not required if the highest stack i		
(m)(m)	(m)	
	0 - 5 km	
Distance from facility to nearest shoreline (km)		
Valley width (km)		
Step 2: Determine the Applicability of the Scre	ening Procedure	
Fill in the following data:		
	Yes	<u>No</u>
•	-	
Is the facility in a valley < km in wid	ith?	
Is the terrain rise within 1 km of the	facility	
greater than the physical stack height	of the	
tallest stack? (Only applies to stacks	; ≥20 meters	
in height)		

Is the distance to the nearest shoreline <5 km? (Only applies to facilities with stacks  $\geq$ 20 meters in height)

For the building listed in Step 1, is the closest property boundary <5 times the building height or <5 times the maximum projected building width? (Only applies to facilities with a stack height <2.5 times the building height)

If the answer is "no" to all the preceding questions, then the HWCAQSP is acceptable. If the answer to any question is "yes", the procedure is not acceptable.

## Step 3: Select the Worst-Case Stack

If the facility has several stacks, a worst-case stack must be chosen to conservatively represent release conditions at the facility. Follow the steps below to identify the worst-case stack.

Apply the following equation to each stack:

## K - HVT

where:

- K = an arbitrary parameter accounting for the relative influence of the stack height and plume rise.
- H = Physical stack height (m)
- $V = Flow rate (m^3/sec)$
- T Exhaust temperature (\*K)

Complete the following table to compute the "K" value for each stack:

Stack No.	Stack height (m)	x	Flow rate (m <sup>3</sup> /sec)	x	Exit temp (*K)	-	K
1		×		x		-	
2		x		x		-	
3		x		x		-	

Select the stack with the lowest "K" value. This is the worst-case stack that will be used for Steps 4 through 9.

Worst-Case Stack is identified as Stack No.

Step 4: Verify Good Engineering Practice (GEP) Criteria

Confirm that the selected worst-case stack meets Good Engineering Practice (GEP) criteria. The stack height to be used in the subsequent steps of this procedure must not be greater than the maximum GEP. Maximum and minimum GEP stack heights are defined as follows:

where:

- H height of the building selected in Step 1 measured from ground level elevation at the base of the stack
- L the lesser dimension of the height or projected width of the building selected in Step 1

Record the following data for the worst-case stack:

Stac	k height (m) =
H(m)	
L(m)	
Then	compute the following:
GEP	(minimum) (m)
GEP	(maximum) (m)

- If the physical height of the worst-case stack exceeds the maximum GEP, then use the maximum GEP stack height for the subsequent steps of this analysis;
- If the physical height of the worst-case stack is less than the minimum GEP, then use generic source number 11 as the selected source for further analysis and proceed directly to Step 6;
- If the physical height of the worst-case stack is between the minimum and maximum GEP, then use the actual physical stack height for the subsequent steps of this analysis.

Step 5: Determine the Effective Stack Height and the Terrain-Adjusted Effective Stack Height (TAESH)

The effective stack height is an important factor in dispersion modeling. The effective stack height is the physical height of the stack plus plume rise. As specified in Step 4, the stack height used to estimate the effective stack height must not exceed GEP requirements. Plume rise is a function of the stack exit gas temperature and flow rate.

In this analysis, the effective stack height is used to select the generic source that represents the dispersion characteristics of the facility. For facilities located in flat terrain and for all facilities with worst-case stacks less than or equal to 10 meters in height, generic source numbers are selected strictly on the basis of effective stack height. In all other cases, the effective stack height is further adjusted to take into account the terrain rise near the facility. This "terrain-adjusted effective stack height" (TAESH) is then used to select the generic source number that represents the dispersion characteristics of the facility. Follow the steps below to identify the effective stack height, the TAESH (where applicable), and the corresponding generic source number.

(A) Go to Table 5.0-1 and find the plume rise value corresponding to the stack temperature and exit flow rate for the worst-case stack determined in Step 3.

Plume	rice	_	(m)
r rume	TISE	_	

(B) Add the plume rise to the GEP stack height of the worst-case stack determined in Steps 3 and 4.

GEP	Stack Height(m)	+	Plume Rise(m)	-	Effective	Stack	Height	(m)
		+		_				

(C) Go to the first column of Table 5.0-2 and identify the range of effective stack heights that includes the effective stack height estimated in Step 5(B). Record the generic source number that corresponds to this range.

0			
Generic	SOUTCE	number :	

- (D) If the source is located in flat terrain<sup>3</sup>, or if the generic source number identified in Step 5(C) above is 1 or 11 (regardless of terrain classification), use the generic source number determined in Step 5(C) and proceed directly to Step 6. Otherwise, continue to Step 5(E).
- (E) For those situations where the conditions in Step 5(D) do not apply, the effective stack height must be adjusted for terrain. The TAESH for each distance range is computed by subtracting the terrain rise within the distance range from the effective stack height.<sup>4</sup>

<sup>&</sup>lt;sup>3</sup>The terrain is considered flat and terrain adjustment factors are not used if the maximum terrain rise within 5 km of the facility (see Step 1) is less than 10 percent of the physical stack height of the worst-case stack.

<sup>\*</sup>Refer to Step 1 for terrain adjustment data. Note that the distance from the source to the outer radii of each range is used. For example, for the range >0.5 - 2.5 km, the maximum terrain rise in the range 0.0 - 2.5 km is used.

>le 5.0-1

ESTIMATED PLUME RISE (IN METERS) BASED ON STACK EXIT FLOW RATE AND GAS TEMPERATURE

Exhaust Temperature (°K)											
Flow Rate (m³/s)	<325	325 - 349	350 - 399	400 - 449	450- 499	500- 599	600 - 699	700- 799	800 - 999	1000 - 1499	>1499
<0.5	0	0	0	0	0	0	0	0	0	0	0
0.5-0.9	ŏ	Ŏ	Ŏ	ŏ	ŏ	ŏ	ŏ	ŏ	ĭ	ĭ	ĭ
1.0-1.9	X	Ŏ	ŏ	ŏ	ĭ	ĭ	2	3	3	3	ā
2.0-2.9	X	Ŏ	1	1	,	7.	6	6	7	Ř	9
	X	1	7	5	č	7	9	10	11	12	
3.0-3.9	Ÿ	7	<i>Z</i>	, 6	8	10	12	13	14	15	13 17
4.0-4.9	Ţ	2	4	0	10	12	14	16	17	19	21
5.0-7.4	2	3	8	12	15	17	20	22	22	23	24
7.5-9.9	3	6	10	15	19	21	23	24	25	26	24 27
10.0-12.4	4	9	12	18	22	23	25	26	27	28	29
12.5-14.9	4	8	13	20	23	24	26	27	28	29	31
15.0-19.9	2	10	17	23	25	27	29	30	31	32	34
20.0-24.9	9		20	25 25	27	29	31	32	33	35	36
25.0-29.9	<b>,</b>	12	20	26	29	31	33	35	36	37	39
30.0-34.9	8	14 16	22 23	28	30	32	35 35	36	30 37	37 39	41
35.0- <b>3</b> 9.9	9	10	23 24	26 29	30 32	32 34	36	38	3 <i>7</i> 39	41	42
40.0-49.9	10	17	24	31	32 34	34 36	39	41	42	44	46
50.0-59.9	12	21	26 27	31	34 36	36 39	42	41	42 45	47	49
60.0-69.9	14	22	2/	33 35	36 38	41	42 44	46	47	47 49	51
70.0-79.9	16	23	29	33	36 40	41	46	48	49	51	54
80.0-89.9	17	25	30	36	40		48	50	51	53	5 <b>6</b>
90.0-99.9	19	26	31	38		44	46 49	50 52	53		
100.0-119.9	21	26	32	39	43	46	49 52	)	56	55 59	58 61
120.0-139.9	22	28	35	42	46	49		55 58	59		
140.0-159.9	23	30	36	44	48	51	55 58			62	65
160.0-179.9	25	31	38	46	50	54		60	62	65	67
180.0-199.9	26	32	40	48	52	56	60	63	65	67	70
>199.9	26	33	41	49	54	58	62	65	67	69	73

Table 5.0-2
SELECTION OF GENERIC SOURCE NUMBER

Effective Stack Height (m)	Generic Source No.
<10.0	1
10.0 - 14.9	2
15.0 - 19.9	3
20.0 - 24.9	4
25.0 - 30.9	5
31.0 - 41.9	6
42.0 - 52.9	7
53.0 - 64.9	8
65.0 - 122.9	9
113.0+	10
Downwash	11

Table 5.0-3
CLASSIFICATION OF LAND USE TYPES

Type <sup>1</sup>	Description	Urban or rural designation <sup>2</sup>
11	Heavy Industrial	Urban
12	Light/Moderate Industrial	Urban
C1	Commercial	Urban
R1	Common Residential (Normal Easements)	Rural
R2	Compact Residential (Single Family)	Urban
R3	Compact Residential (Multi-Family)	Rural
R4	Estate Residential (Multi-Acre Plots)	Rural
A1	Metropolitan Natural	Rural
A2	Agricultural	Rural
A3	Undeveloped (Grasses/Weeds)	Rural
A4	Undeveloped (Heavily Wooded)	Rural
A5	Water Surfaces	Rural

- EPA, Guideline on Air Quality Models (Revised), EPA-450/2-78-027, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, July, 1986.
- 2. Auer, August H. Jr., "Correlation of Land Use and Cover with Meteorological Anomalies," <u>Journal of Applied Meteorology</u>, pp. 636-643, 1978.

Distance Range (km)	Effective Stack Height (m) [see Step 5(B)]	-	Maximum Terrain Rise (m) (see Step 1)	•	TAESH(m)
0.0 - 0.5		-		-	
>0.5 - 2.5		-		-	
>2.5 - 5.0		-		-	

If the terrain rise for any of the distance ranges is greater than the effective stack height, set the TAESH equal to zero and use generic source number 1 for that distance range.

Record the generic source numbers from Table 5.0-2 based on each of the TAESH values.

Distance Range(km)	Generic Source No. (after terrain adjustment)
0.0 - 0.5	,
>0.5 - 2.5	
>2.5 - 5.0	<del></del>

Step 6: Classify the Site as Urban or Rural

(A) Classify the land use near the facility as either urban or rural by determining the percentage of urban land use types (as defined in

Table 3; for further guidance see the footnoted references) that fall within 3 km of the facility.<sup>5</sup>

Method Used to Estimate Percent Urban Land Use:	Visual	Planimeter
		<del></del>
Estimated Percentages	Urban	Rural

If the urban land use percentage is less than or equal to 30 percent based on a visual estimate, or 50 percent based on a planimeter, the local land use is considered rural. Otherwise, the local land use is considered urban.

Classification	Urban	Rural
(check applicable space)		

(B) Based on the TAESH and the urban/rural classification of surrounding land use, use the following table to determine the threshold distance between any stack and the nearest facility boundary.

The delineation of urban and rural areas, can be difficult for the residential-type areas listed in Table 5.0-3. The degree of resolution in Table 5.0-3 for residential areas often cannot be identified without conducting site area inspections. This process can require extensive analysis, which, for many applications, can be greatly streamlined without sacrificing confidence in selecting the appropriate urban or rural classification. The fundamental simplifying assumption is based on the premise that many applications will have clear-cut urban/rural designations, i.e., most will be in rural settings that can be definitively characterized through a review of aerial photographs, zoning maps, or U.S. Geological Survey topographical maps.

Terrain adjusted effective stack height range (m)	Distance (m)		
	Urban	Rural	
1 - 9.9	200	200	
10 - 14.9	200	250	
15 - 19.9	200	250	
20 - 24.9	200	350	
25 - 30.9	200	450	
31 - 41.9	200	550	
42 - 52.9	250	800	
53 - 64.9	300	1000	
65 - 112.9	400	1200	
113+	700	2500	

Record	the	following	information:
VECOLO	CITE	TOTTOMINE	THITOTIME CTOH.

Threshold distance	from the t	table (m):		
Minimum distance fr	rom any sta	ack to property	boundary (m):	<u> </u>

If the minimum distance between any stack and the nearest facility boundary is greater than the threshold distance, the surrounding buffer distance is considered significant and the facility is likely to benefit from use of the HWCAQSP relative to the Tier I and II limits (see discussion of benefits from using HWCAQSP in Introduction section).

## Step 7: Determine Maximum Dispersion Coefficients

(A) Determine maximum average hourly dispersion coefficients. Based on the results of Step 6(A), select either Table 5.0-4 (urban) or Table 5.0-5 (rural) to determine the maximum average hourly dispersion coefficient. For flat terrain [defined in Step 5(D)] and for all sites with

<sup>&</sup>lt;sup>6</sup>For the distance range 6 to 20 kilometers, generic source number 1 is used to conservatively represent the maximum dispersion coefficient.

generic source numbers 1 or 11, use Step 7(A)(1). For rolling or complex terrain (excluding generic sources number 1 and 11), use Step 7(A)(2).

(1) Search down the appropriate generic source number column [based on Step 5(C)], beginning at the minimum fenceline distance listed in Step 6(B). Record the maximum average hourly dispersion coefficient encountered.

Maximum	Average	Hourly	Dispersion	Coefficient		$(\mu g/m^3/g/sec$	:)
---------	---------	--------	------------	-------------	--	--------------------	----

(2) For each of the three distance-based generic source numbers listed in Step 5(E), search down the appropriate generic source number columns, beginning at the minimum fenceline distance listed in Step 6(B). Note that different columns may be used for each of the three distance ranges if there is a need for terrain adjustment. Record the maximum dispersion coefficient for each generic source number.

Distance Range (km)	Generic Source No. [from Step 5(E)]	Maximum Dispersion Coefficient $(\mu g/m^3/m/sec)$
0.0 - 0.5	<del></del>	
>0.5 - 2.5		
>2.5 - 5.0		
>5.0 - 20.0	1	

<sup>&</sup>lt;sup>7</sup>Exclude all distances that are closer to the facility than the property boundary. For example, if the actual distance to the nearest property boundary is 265 meters, begin at the 300 meter distance in Tables 5.0-4 and 5.0-5.

Table 3.0-4

ISCT PREDICATED MAXIMUM CONCENTRATIONS (UG/M')\* FOR HAZARDOUS WASTE COMBUSTORS USING URBAN CONDITIONS

Distance (KM)	Generic Source #1 (<10M)	Generic Source #2 (10 M)	Generic Source #3 (15 M)	Generic Source #4 (20 M)	Generic Source #5 (25 M)	Generic Source #6 (31 M)	Generic Source #7 (42 M)	Generic Source #8 (53 M)	Generic Source #9 (65 M)	Generic Source #10 (113 M)	Generic Source #11 (Downwash
0.20	680.1	517.5	368.7	268.7	168.5	129.8	63.4	30.1	18.4	1.6	662.3
0.25	521.9	418.2	303.7	232.6	163.D	124.2	67.6	38.5	19.8	3.2	500.0
0.30	407.7	351.7	256.2	199.0	147.0	118.3	63.5	41.5	25.0	4.2	389.3
0.35	326.2	304.2	221.6	172.7	130.2	107.9	60.0	40.5	27.3	5.4	311.9
0.40	268.5	268.5	195.6	152.5	115.7	97.1	59.6	37.8	27.4	5.8	268.
0.45	240.8	240.7	175.4	136.7	103.9	87.6	56.6	37.2	26.3	5.8	240.1
0.50	218.5	218.5	159.2	124.1	94.4	79.7	52.9	36.7	24.7	5.8	218.
0.55	200.3	200.3	145.9	113.8	86.5	73.1	49.2	35.4	24.5	6.6	200.
0.60	185.1	185.1	134.9	105.1	80.0	67.6	45.8	33.8	24.3	7.1	185.
0,65	172.2	172.2	125.5	97.8	74.4	62.9	42.7	32.0	23.7	7.4	172.
0.70	161.2	161.2	117.4	91.6	69.6	58.9	40.1	30.2	22.9	7.5	161.
0.75	151.6	151.6	110.5	86.1	65.5	55.4	37.7	28.6	22.0	7.5	151.
0.80	143.2	143.2	104.4	81.4	61.9	52.3	35.6	27.1	21.1	7.4	143.
0.85	135.8	135.8	99.0	77.2	58.7	49.6	33.8	25.7	20.2	7.2	135.
0.90	129.2	129.2	94.2	73.4	55.8	47.2	32.1	24.5	19.3	7.0	129.
0.95	123.3	123.3	89.9	70.1	53.3	45.0	30.7	23.4	18.5	6.8	123.
1.00	118.0	118.0	86.0	67.0	51.0	43.1	29.4	22.4	17.7	6.5	118.
1.10	108.8	108.0	79.3	61.8	47.0	39.7	27.1	20.6	16.4	6.5	108.
1.20	101.1	101.1	73.7	57.4	43.7	36.9	25.2	19.2	15.2	6.4	101.
1.30	94.6	94.6	68.9	53.7	40.9	34.5	23.5	18.0	14.2	6.3	94.
1.40	89.0	89.0	64.8	50.6	38.5	32.5	22.1	16.9	13.4	6.1	89.
1.50	84.1	84.1	61.3	47.8	36.3	30.7	20.9	16.0	12.7	5.9	84.
1.60	79.8	79.8	58.2	45.4	34.5	29.2	19.9	15.2	12.0	5.6	79.
1.70	76.0	76.0	55.4	43.2	32.9	27.8	18.9	14.4	11.4	5.4	76.
1.80	72.7	72.7	53.0	41.3	31.4	26.5	18.1	13.8	10.9	5.2	72.
1.90	69.6	69.6	50.7	39.6	30.1	25.4	17.3	13.2	10.5	5.0	69.
2.00	66.9	66.9	48.8	38.0	28.9	24.4	16.7	12.7	10.1	4.8	66.
2.25	61.1	61.1	44.5	34.7	26.4	22.3	15.2	11.6	9.2	4.4	61.
2.50	56.4	56.4	61.1	32.1	24.4	20.6_	14.0	10.7	8.5	6.1	56.
2.75	52.6	52.6	38.3	29.9	22.7	19.2	10.0	10.0	7.9	3.8	52.
3,00	49.3	49.3	35.9	28.0	21.3	18.0	9.4	9.4	7.4	3.6	49.
4.00	40.2	40.2	29.3	22.8	17.4	14.7	7.6	7.6	6.1	2.9	40.
5.00	34.5	34.5	25.2	19.6	16.9	12.6	6.6	6.6	5.2	2.5	34.
6.00	30.7	30.7	30.7	30.7	30.7	30.7	30.7	30.7	30.7	30.7	30.
7.00	27.8	27.8	27.8	37.8	27.8	27.8	27.8	27.8	27.8	27.8	27.
8.00	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.
9.00	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.
10.00	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.
15.00	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.
20.00	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.01	15.

Based on a 1 Gram/Second Emission Rate

Table 5.0-5

1SCT PREDICATED MAXIMUM CONCENTRATIONS (UG/M')\* FOR HAZARDOUS WASTE COMBUSTORS USING RURAL CONDITIONS

Distance (KM)	Generic Source #1 (<10H)	Generic Source #2 (10 M)	Generic Source #3 (15 M)	Generic Source #4 (20 M)	Generic Source #5 (25 M)	Generic Source #6 (31 M)	Generic Source #7 (42 M)	Generic Source #8 (53 M)	Generic Source #9 (65 M)	Generic Source #10 (113 M)	Generic Source #11 (Downwash)
0.20	1771.1	670.3	308.6	176.8	102.8	76.5	28.0	10.1	3.5	0.0	1350.8
0.25	1310.6	678.4	316.9	183.6	104.6	71.8	38.0	17.6	7.9	0.2	1227.3
0.30	1002.3	629.2	303.4	199.1	100.4	75.0	39.7	24.0	12.6	0.8	1119.3
0.35	798.4	569.6	282.3	200.7	117.0	71.1	36.3	25.9	16.8	1.9	1023.8
0.40	656.9	516.5	278.7	194.4	125.2	82.7	25.3	24.6	18.1	3.1	938.9
0.45	621.5	471.1	277.6	184.3	127.5	89.7	35.6	21.7	17.6	4.3	851.8
0.50	633.5	432.4	272.0	172.7	125.7	92.9	34.4	21.6	15.9	5.5	787.8
0.55	630.1	399.2	263.8	. 168.0	121.6	93.3	38.6	22.1	13.6	6.5	730.6
0.60	616.6	370.4	254.0	169.1	116.2	91.8	42.6	21.7	14.3	6.7	676.4
0.65	596.7	345.4	243.6	168.1	110.3	89.2	45.3	20.9	14.7	6.4	633.4
0.70	573.2	323.4	232.9	165.6	104.5	85.8	47.0	23.3	14.6	5.9	592.0
0.75	546.9	304.0	222.3	162.0	98.8	82.2	47.7	25.5	14.3	5.5	<b>554.6</b> ;
0.80	520.9	286.8	212.1	157.7	98.8	78.5	47.8	27.1	13.8	5.1	522.1
0.85	495.7	271.5	202.4	153.0	99.0	74.9	47.4	28.3	15.0	4.7	491.8
0.90	471.5	257.8	193.3	148.1	98.6	71.4	46.6	29.1	16.3	4.5	464.2
0.95	448.5	245.4	184.7	143.1	97.6	72.3	45.6	29.6	17.3	4.2	438.9
1.00	426.8	234.2	176.8	138.1	96.3	72.6	44.4	29.8	18.2	4.0	415.8
1.10	387.5	214.7	162.5	128.2	91.9	71.1	41.8	29.5	19.3	3.9	375.0
1.20	353.5	198.4	150.3	119.3	87.4	69.1	39.1	28.6	19.8	4.1	340.3
1.30	323.0	189.6	139.9	111.5	82.9	66.7	36.6	27.5	19.8	4.2	310.4
1.40	296.6	182.2	130.8	104.5	78.7	64.2	34.3	26.2	19.5	4.2	284.6,
1.50	273.3	174.6	122.9	98.3	74.7	61.6	32.3	24.9	19.0	4.2	262.0
1.60	252.7	167.0	115.9	92.8	71.0	59.1	31.8	23.6	18.4	4.2	242.2
1.70	234.5	159.6	109.7	87.9	67.6	56.7	31.6	22.5	17.7	4.3	224.7
1.80	218.3	152.4	104.1	83.5	64.4	54.3	31.3	21.4	17.0	4.5	211.9
1.90	203.7	145.6	99.1	79.5	61.5	52.1	30.9	20.4	16.3	4.8	198.4
2.00	190.7	139.1	94.6	75.9	58.8	50.0	30.4	19.5	15.7	5.1	186.3
2.25	164.4	124.5	85.1	68.3	53.0	45.4	28.9	18.1	14.2	5.4	160.8
2.50	163.7	112.1	77.3	62.1	48.2	41.4	27.2	17.9	12.9	5.5	140.7
2.75	127.0	101.5	70.9	56.9	38.1	38.1	25.6	17.5	11.8	5.4	124.5
3.00	113.4	92.4	65.6	52.6	35.2	35.2	24.0	17.0	11.2	5.2	112.5
4.00	78.8	67.3	50.6	40.6	27.2	27.2	29.0	14.3	10.4	4.3	78.3
5.00	59.1	56.6	61.6	33.2	22.2	22.2	15.6	12.0	9.3	3.5	58.8_
6.00	56.7	46.7	46.7	46.7	46.7	46.7	46.7	46.7	46.7	46.7	46.7
7.00	40.4	40.4	40.4	40.4	40.4	40.4	40.4	40.4	40.4	40.4	40.4
8.00	35.8	35.8	35.8	35.8	35.8	35.8	35.8	35.8	35.8	35.8	35.8
9.00	32.2	32.2	32.2	32.2	32.2	32.2	32.2	32.2	32.2	32.2	32.2
10.00	9.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4
15.00	20,5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
20.00	15.9	15.9	15.9	15.9	15.9	15.9	15.9	15.9	15.9	15.9	15.9

"Based on a 1 Gram/Second Emission Rate

- (B) Determine annual/hourly ratio for rural analysis. The maximum average annual dispersion coefficient is approximated by multiplying the maximum hourly dispersion coefficient (identified in Step 7(A) by the appropriate ratio selection from Table 6. The generic source number(s) [from Steps 5(C) or 5(E)], urban/rural designation (from Step 6), and the terrain type are used to select the appropriate scaling factor. Use the noncomplex terrain designation for all sources located in flat terrain, for all sources where the physical stack height of the worst-case stack is less than or equal to 10 m, for all sources where the worst-case stack is less than the minimum GEP, and for those sources where all of the TAESH values in Step 5(E) are greater than zero. Use the complex terrain designation in all other situations.
- (C) Determine maximum average annual dispersion coefficient. The maximum average annual dispersion coefficient is determined by multiplying the maximum hourly dispersion coefficient [Step 7(A)] by its corresponding annual/hourly ratio [Step 7(B)].

Terrain	Distance from Stack (m)	Generic Source Number	Maximum Hourly Dispersion Coefficient (μg/m³/g/sec)	Annual/ Hourly Ratio	Maximum Annual Dispersion Coefficient (µg/m³/g/sec)¹
Flat	0 - 20.0				
	0 - 0.5				
	>0.5 -2.5				
Rolling	>2.5 -5.0				
or Complex	>5.0 - 20.0				

<sup>&</sup>lt;sup>1</sup>Maximum hourly dispersion coefficient times annual/hourly ratio.

- Step 8: Estimate Maximum Ambient Air Concentrations see procedures prescribed in subpart H of 40 CFR Part 266.
- Step 9: Determine Compliance with Regulatory Limits see procedures prescribed in subpart H of 40 CFR Part 266.

## Step 10: Multiple Stack Method (Optional)

This option is a special case procedure that may be helpful when (1) the facility exceeded the regulatory limits for one or more pollutants, as detailed in Step 9, and (2) the facility has multiple stacks with substantially different emission rates and effective release heights. Only those pollutants that fail the Step 9 screening limits need to be addressed in this exercise.

This procedure assesses the environmental impacts from each stack and then sums the results to estimate total impacts. This option is conceptually the same as the basic approach (Steps 1 through 9) and does not involve complex calculations. However, it is more time-consuming and is recommended only if the basic approach fails to meet the risk criteria. The procedure is outlined below.

## (A) Compute effective stack heights for each stack.8

Stack No.	GEP Stack height (m)	Flow rate (m³/sec)	Exit temp (*K)	Plume rise (m)	Effective stack height (m)
1					<del></del>
2	<del></del>				
3	***********	<del></del>			<del></del>

Add an additional page if more than three stacks are involved. Circle the maximum and minimum effective stack heights.

Follow the procedure outlined in Step 4 of the basic screening procedure to determine the GEP for each stack. If a stack's physical height exceeds the maximum GEP, use the maximum GEP values. If a stack's physical height is less than the minimum GEP, use generic source number 11 in the subsequent steps of this analysis. Follow the procedure in Steps 5(A) and 5(B) to determine the effective height of each stack.

(B) Determine if this multiple-stack screening procedure will likely produce less conservative results than the procedure in Steps 1 through 9. To do this, compute the ratio of maximum-to-minimum effective stack height:
Maximum Effective Stack Height Minimum Effective Stack Height
If the above ratio is greater than 1.25, proceed with the remaining steps. Otherwise, this option is less likely to significantly reduce the degree of conservatism in the screening method.
(C) Determine if terrain adjustment is needed and select generic source numbers. Select the shortest stack height and maximum terrain rise out to 5 km from Step 1 and determine if the facility is in flat terrain.
Shortest stack height (m) =  Maximum terrain rise in meters out to 5 km =
Terrain Rise (m) x 100
If the value above is greater than 10 percent, the terrain is considered nonflat; proceed to Step 10(D). If the ratio is less than or equal to 10 percent, the terrain is considered flat. Identify the generic source numbers based on effective stack heights computed in Step 10(A). Refer to Table 5.0-2 provided earlier to identify generic source numbers. Record the generic source numbers identified and proceed to Step 10(F).
Stack No. 1 2 3
Generic Source Numbers

- (D) Compute the TAESH and select generic source numbers (four sources located in nonflat terrain).
- 1. Compute the TAESH for all remaining stacks using the following equation:

HE - TR - TAESH

where:

HE - effective stack height (m)

TR - maximum terrain rise for each distance range (m)

TAESH - terrain-adjusted effective stack height (m)

Use the table below to calculate the TAESH for each stack.9

		Distance Range (km)					
	0 - 0.5	<u>&gt;0.5 - 2.5</u>	<u>&gt;2.5 - 5.0</u>				
Stack No.	HE - TR - TAESH	HE - TR = TAESH	HE - TR - TAESH				
1	· •	·					
2		· •					
3		· •	· •				

For those stacks where the terrain rise within a distance range is greater than the effective stack height (i.e., HE - TR is less than zero), the TAESH for that distance range is set equal to zero, and generic source number 1 should be used for that distance range for <u>all</u> subsequent distance ranges. Additionally, for all stacks with a physical stack height of less than or

 $<sup>^{9}</sup>$ Refer to Step 1 for terrain adjustment data. Note that the distance from the source to the outer radii of each range is used. For example, for the range >0.5 - 2.5 km, the maximum terrain rise in the range 0.0 - 2.5 km is used.

equal to 10 meters, use generic source number 1 for all distance ranges. <sup>10</sup> For the remaining stacks, proceed to Step 10(D)(2).

2. For the remaining stacks, refer to Table 5.0-2 and, for each distance range, identify the generic source number that includes the TAESH. Use the values obtained from Steps 10(D)(1) and 10(D)(2) to complete the following summary worksheet;

Generic Source Number After Terrain Adjusted (if needed)

Stack No.	0 - 0.5 km	>0.5 - 2.5 km	>2.5 - 5.0 km
1			
2		**************************************	
3		-	

(E) Identify maximum average hourly dispersion coefficients. Based on the land use classification of the site (e.g., urban or rural), use either Table 5.0-4 or Table 5.0-5 to determine the appropriate dispersion coefficient for each distance range for each stack. Begin at the minimum fenceline distance indicated in Step 7(B) and record on Worksheet 5.0-1 the dispersion coefficient for each stack/distance range. For stacks located in facilities in flat terrain, the generic source numbers were computed in Step 10(C). For stacks located in facilities in rolling and complex terrain, the generic source numbers were computed in Step 10(D). For flat terrain applications and for stacks with a physical height of less than or equal to 10 meters, only one generic source number is used per stack for all distance ranges. For other situations up to three generic source numbers may be needed per stack (i.e., a unique generic source number per distance range). In Tables 5.0-4 and 5.0-5, the dispersion coefficients for distances of 6 km to 20 km are the same for

<sup>&</sup>lt;sup>10</sup>This applies to all stacks less than or equal to 10 meters regardless of the terrain classification.

Worksheet 5.0-1 Dispersion Coefficient by Downwind Distance<sup>1</sup>

	المرادين المراقب النصافية المراسيين بالمراسية		
E Distance	Stack 1	Stack 2	Stack 3
0.20			
0.25			
0.30	 		
0.35	 		
0.40			
0.45			
0.50			
0.55			
0.60			
0.65			
0.70			
0.75			
0.80			
0.85			
0.90			
0.95			
1.00			
1.10			
1.20			
1.30			
1.40			
1.50			
1.60			
1.70			
1.80			
1.90			
2.00			
2.25			
2.50		<u> </u>	
2.75			
3.00			
4.00			
5.00			
6.00			
7.00			
8.00	<u> </u>		
9.00		<u> </u>	ļ
10.00		<u> </u>	<u></u>
15.00			
20.00	<u> </u>		1

<sup>&</sup>lt;sup>1</sup>Note: This procedure places all stacks at the same point, but allows for consideration of different effective stack heights. The distance to the closest boundary (extracted from Step 1) should be the closest distance to any stack.

all generic source numbers in order to conservatively represent terrain beyond 5 km (past the limits of the terrain analysis).

(F) Estimate maximum hourly ambient air concentrations. In this step, pollutant-specific emission rates are multiplied by appropriate dispersion coefficients to estimate ambient air concentrations. For each stack, emissions are multiplied by the dispersion coefficient selected in Step 10(E) and summed across all stacks to estimate ambient air concentrations at various distances from the facility. From these summed concentrations, the maximum hourly ambient air concentration is selected. First, select the maximum emission rate of the pollutant. Record these data in the spaces provided below. 12

## Maximum Annual Emission Rates (g/sec)

			<del></del>
Pollutant	Stack 1	Stack 2	Stack 3

Complete a separate copy of Worksheet 5.0-2 for each pollutant and select the highest hourly concentration from the summation column at the far right of the worksheet. Record the maximum hourly air concentration for each pollutant analyzed (add additional lines if needed):

<u>Pollutant</u>	Maximum Hourly Air Concentration
<del></del>	

<sup>11</sup>Recall that it is recommended that this analysis be performed for only one or two pollutants. The pollutants chosen for this analysis should be those that show the most significant exceedances of the risk threshold.

<sup>&</sup>lt;sup>12</sup>Refer to Step 8 of the basic screening procedure. At this point in the screening procedure, annual emissions are used to represent hourly average emission rates. These values will be adjusted by the annual/hourly ratio to estimate annual average concentrations.

## Worksheet 5.0-2 Maximum Hourly Ambient Air Concentration

Pollutant

Total Distance (km)	Stack 1 ER x DC = C	Stack 2 ER x DG = C	Stack 3 ER x DG = C	Summed Concentration from all Stacks
0.20	×	×=	x=	
0.25		*=	*	
0.30	=	×		J
0.35	*		*	
0,40	×	=		
0.45		×	×	
<b>0.5</b> 5	·		×	<b> </b>
0.55	*	*	* *	]
0.60			×	<u> </u>
0.45		*	*	ļ
0.70	×		×	ļ ———
0.80	**************************************	*		
0.85		*	*	
0.90	*	*	×	·
0.95 1.00				
1.10				
1.10				
1.20				
1.40				
1.50				

ER= Annual Average Emission Rate
DC= Hourly Dispersion Coefficient (from Worksheet 5.0-1)
C= Estimated Maximum Hourly Ambient Air Concentration

Pollutant	

Total Distance (km)	Stack 1	Stack 2 ER x DC = C	Stack 3 ER x DC = C	Summed Concentration from all Stacks
1.60	x	**	x	_
1.70		×	×	_
1.00	*	*	×	
1.90		*	* *	
2.00	* *	* *	×	_
2.25		*	* =	-
2.50		*		
3.75		* *	×	-
3.00 4.00				-
5.00			×	-
6.00		* -		-
7.00		× -	×	
<b>a</b> .00			x =	
9.00	x	* -	x -	
10.00			*	
15.00		*	* *	
20.00		**	* -	

ER=Annual Average Emission Rate
DC= Hourly Dispersion Coefficient (from Worksheet 5.0-1)
C= Estimated Maximum Hourly Ambient Air Concentration

5-25

## Worksheet 5.0-2 Maximum Ambient Air Concentration

Pollutant

Total Distance (km)	Stack 1	Stack 2 ER x DC = C	Ştack 3 ER x DÇ = C	Summed Concentration from all Stacks
1.60	<u> </u>	* *	* *	
1.70	×	*	\ *	_
1.00			*	_
1.90		\ * •	×	
2.00		*	×	
2.25		*	*	_
2.50		*		_
2.75		* *		-
3.00		*	* *	-
4.00		**	*	_
5.00			×	-
6.00	×	*	*	- [
7.00	×	*		_
<b>#.</b> 00	*		·	-
9,00 .	*		\ * *	-
10,00				-
15.00		×	* =	- }
20.00		x =	*	_

ER - Annual average emission rate

DC = Hourly dispersion coefficient (from Worksheet 1)

C = Estimated maximum hourly ambient air concentration

(G) Determine the complex/noncomplex designation for each stack. For each stack, subtract the maximum terrain rise within 5 km of the site from the physical stack height and designate the stack as either complex or noncomplex. If the stack height minus the maximum terrain rise (within 5 km) is greater than zero or if the stack is less than 10 meters in physical height, then assign the stack a noncomplex designation. If the stack height minus the maximum terrain rise (within 5 km) is less than or equal to zero, then assign the stack a complex designation.

Perform the following computation for each stack and record the information in the spaces provided. Check in the spaces provided whether the stack designation is complex or noncomplex.

Stack No.	Stack Height (m)	Maximum Terrain Rise (m)		Co	mplex	Noncomplex
1		•		_(m)		
2		•		_(m)		
3			•	_(m)		-

(H) Identify annual/hourly ratios. Extract the annual/hourly ratios for each stack by referring to Table 5.0-6. Generic source numbers (from Steps 10(C) or 10(D), urban/rural designation (from Step 6), and complex or noncomplex terrain designations (from Step 10(G)) are used to select the appropriate scaling factor needed to convert hourly maximum concentrations to estimates of annual average concentrations.

Complete the following table; 13

Stack No.	Generic Source No. Steps 10 (C or D)		Annual/hourly ratio (from Table 5.0-6)			
	Dis	tance ranges	(km)	Dis	tance range	s (km)
	0-0.5	>0.5-2.5	>2.5-5.0	0-0.5	>0.5-2.5	>2.5-5.0
1						
2						
3						

- (I) Select the highest annual/hourly ratio among all of the stacks, 14 and then estimate the maximum annual average ambient air concentrations for each pollutant by completing the following table, where:
  - C Maximum total hourly ambient air concentration  $(\mu g/m^3)$  for pollutant "N" from Step 10(F),
  - $C_a$  = Maximum annual average air concentration for pollutant "N"  $(\mu g/m^3)$ ,
  - R Annual/hourly ratio.

<sup>&</sup>lt;sup>13</sup>If any stack (excluding generic stack number 1 and 11) in Step 10(D) shows a negative terrain adjusted stack height, use the complex terrain annual/hourly ratios.

<sup>14</sup>As an option, the user can identify the stack with the highest ratio for each distance range (rather than the absolute highest). In this case, extra sheets would be needed to show estimated annual average concentrations from each stack by multiplying emission rate times maximum hourly dispersion coefficient times maximum annual/hourly ratio for applicable distance range. Then sum across all stacks for each downwind distance.

Table 5.0-6

95TH PERCENTILE OF ANNUAL/HOURLY RATIOS

	Noncomplex To	errain		Complex Ter	rain
Source	Urban	Rural	Source	Urban	Rural
1 2 3 4 5 6 7 8 9 10 11	0.019 0.033 0.031 0.029 0.028 0.028 0.031 0.030 0.029 0.029	0.014 0.019 0.018 0.017 0.017 0.015 0.013 0.011 0.008 0.015	1 2 3 4 5 6 7 8 9 10	0.020 0.020 0.030 0.051 0.067 0.059 0.036 0.026 0.026	0.053 0.053 0.057 0.047 0.039 0.034 0.031 0.024 0.024 0.013

Pollutant	C (μg/m)	x	R -	$C_a (\mu g/m^3)$
		×		
		x		

(J) Use the maximum annual average concentrations from Step 10(I) to determine compliance with regulatory requirements.

#### Section 6.0

## SIMPLIFIED LAND USE CLASSIFICATION PROCEDURE FOR COMPLIANCE WITH TIER I AND TIER II LIMITS

## 6.1 Introduction

This section provides a simplified procedure to classify areas in the vicinity of boilers and industrial furnance sites as urban or rural in order to set risk-based emission limits under subpart H of 40 CFR Part 266. Urban/rural classification is needed because dispersion rates differ between urban and rural areas and thus, the risk per unit emission rate differs accordingly. The combination of greater surface roughness (more buildings/structures to generate turbulent mixing) and the greater amount of heat released from the surface in an urban area (generates buoyancy-induced mixing) produces greater rates of dispersion. The emission limit tables in the regulation, therefore, distinguish between urban and rural areas.

EPA guidance (EPA 1986) provides two alternative procedures to determine whether the character of an area is predominantly urban or rural.

One procedure is based on land use typing and the other is based on population density. Both procedures require consideration of characteristics within a 3-km radius from a source, in this case the facility stack(s). The land use typing method is preferred because it more directly relates to the surface characteristics that affect dispersion rates. The remainder of this discussion is, therefore, focused on the land use method.

While the land use method is more direct, it can also be laborintensive to apply. For this discussion, the land use method has been
simplified so that it is consistent with EPA guidance (EPA 1986; Auer 1978),
while streamlining the process for the majority of applications so that a
clear-cut decision can be made without the need for detailed analysis. Table
6.0-1 summarizes the simplified approach for classifying areas as urban or
rural. As shown, the applicant always has the option of applying standard
(i.e., more detailed) analyses to more accurately distinguish between urban
and rural areas. However, the procedure presented here allows for simplified
determinations, where appropriate, to expedite the permitting process.

Table 6.0-1

CLASSIFICATION OF LAND USE TYPES

Type <sup>1</sup>	Description	Urban or rural designation <sup>2</sup>	
11	Heavy Industrial	Urban	
12	Light/Moderate Industrial	Urban	
Cl	Commercial	Urban	
R1	Common Residential (Normal Easements)	Rural	
R2	Compact Residential (Single Family)	Urban	
R3	Compact Residential (Multi-Family)	Urban	
R4	Estate Residential (Multi-Acre Plots)	Rural	
A1	Metropolitan Natural	Rural	
A2	Agricultural	Rural	
. A3	Undeveloped (Grasses/Weeds)	Rural	
, A4	Undeveloped (Heavily Wooded)	Rural	
A5	Water Surfaces	Rural	

- 1. EPA, Guideline on Air Quality Models (Revised), EPA-450/2-78-027, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, July, 1986.
- Auer, August H. Jr., "Correlation of Land Use and Cover with Meteorological Anomalies," <u>Journal of Applied Meteorology</u>, pp. 636-643.
   1978.

## 6.2 Simplified Land Use Process

The land use approach considers four primary land use types: industrial (I), commercial (C), residential (R), and agricultural (A). Within these primary classes, subclasses are identified, as shown in Table 6.0-1. The goal is to estimate the percentage of the area within a 3-km radius that is urban type and the percentage that is rural type. Industrial and commercial areas are classified as urban; agricultural areas are classified as rural.

The delineation of urban and rural areas, however, can be more difficult for the residential type areas shown in Table 6.0-1. The degree of resolution shown in Table 6.0-1 for residential areas often cannot be identified without conducting site area inspections and/or referring to zoning maps. This process can require extensive analysis, which, for many applications, can be greatly streamlined without sacrificing confidence in selecting the appropriate urban or rural classification.

The fundamental simplifying assumption is based on the premise that many applications will have clear-cut urban/rural designations, i.e., most will be in rural settings that can be definitively characterized through a brief review of topographical maps. The color coding on USGS topographical maps provides the most effective means of simplifying the typing scheme. The suggested typing designations for the color codes found on topographical maps are as follows:

Green Wooded areas (rural).

White areas generally will be treated as rural. This code applies to areas that are unwooded and do not have densely packed structures which would require the pink code (house omission tint). Parks, industrial areas, and unforested rural land will appear as white on the topographical maps. Of these categories, only the industrial areas could potentially be classified as urban based on EPA 1986 or Auer 1978. Industrial areas can be easily identified in most cases by the characteristics shown in Figure 6.0-1. For this simplified procedure, white areas that have an industrial classification will be treated as urban areas.

## Figure 6.0-1

# Supplementary Publication Symbols

117	Single track	
**/	Line designs 000" Tie designs 000" engsh 04", seause 20" center to center	
118	Single track abandoned	484~00~€0
119	Single track under construction	
120	Multiple main line track  Overst with 817 Line weight 007 Fe rength 007 seems 307 center to center if more than two tracks laser, with double creases at some of change. Double creases .017 overst width.	2 784G#2
121	Multiple track abandoned	
122	Multiple track under construction Some as existing track with seare SP, dash SP Least Under Construction	
123	Juxtaposition	
124	Railroad in street	
125	Yards	
126	Sidings	
176	Cutting anger (SEP street ander excess 30° needs of of anger to suiting in NE excepts, inter 60° todays (SP contex to contex).	:==:22 \$
4	Sewage disposal or filtration plant_ }	
	Tanks: oil, gas, water. etc	
	Tanks: oil, gas, water, etc.	C 🗇 an

## STATISTICAL METHODOLOGY FOR BEVILL RESIDUE DETERMINATIONS

This section describes the statistical comparison of waste-derived residue to normal residue for use in determining eligibility for the Bevill exemption under 40 CFR 266.112.

#### 7.1 Comparison of Waste-derived Residue with Normal Residue

To meet the special criteria under part 266.112(b)(1), waste-derived residue must not contain Appendix VIII, Part 261, constituents (toxic constituents) at concentrations significantly higher than in residue generated without burning or processing hazardous waste. Concentrations of toxic constituents in normal residue are determined based on analysis of a minimum of 10 composite samples. (Note that "normal" residue refers to residue generated by a facility when operating without burning hazardous waste.) The 95th percent confidence interval about the mean of the normal residue concentrations must be used in the comparison of waste-derived residue with normal residue: the confidence interval is determined as described in Section 7.2 below. The concentration of a toxic constituent in the waste-derived residue is not considered to be significantly higher than in the normal residue if the concentration in the waste-derived residue does not exceed the upper 95th percent confidence interval about the mean that was established for the normal residue. Concentrations of toxic constituents in waste-derived residue are determined based on analysis of samples taken over a compositing period of not more than 24 hours.

## 7.2 <u>Calculation of the 95th Percent Confidence Interval About the Mean</u> <u>for Toxic Constituents in Normal Residue</u>

The 95th percent confidence interval about the mean is calculated for a set of values using a "t" distribution. In use of the "t" distribution, it is assumed that the values are normally distributed; the "t" distribution is applicable for use with small sample sets (i.e. approximately 10-30

samples). The 95th percent confidence interval about the mean is determined using the following equation:

95th percent confidence interval = 1 X  $\pm$  t<sub>-/2</sub> (s/ $\sqrt{n}$ )

where X = mean of the normal residue concentrations,  $X = \frac{\sum_{i=1}^{n} X_i}{n}$ 

= = the level of significance = 0.05,

s - standard deviation of the normal residue concentrations,

$$s = \sum_{i=1}^{n} (X_i - \overline{X})^2 / (n-1)^{-1/2}$$
, and

n - sample size.

The values of the "t" distribution at the  $\infty/2$  level of significance and n-1 degrees of freedom are given in Table 7.0-1.

For example, a normal residue test results in 10 samples with the following analysis results for toxic compound A:

Sample <u>Number</u>	Concentration of Compound A (ppm)
1	10
2	10
3	15
4	10
5	7
6	12
7	10
8	16
9	15
10	10

The mean and standard deviation of these measurements, calculated using equations above, are 11.5 and 2.9 respectively. Assuming that the values are normally distributed, the upper 95th percent confidence interval value about the mean is given by:

Table 7.0-1

# t DISTRIBUTION VALUES

degrees of freedom (n-1)	Percentage Point of t Distribution $2/2 = 0.025$
1	12.706
2	4.303
3	3.182
4	2.776
5	2.571
6	2.447
7	2.365
8	2.306
9	2.262
10 11 12 13	2.228 2.201 2.179 2.160 2.145
15	2.131
16	2.120
17	2.110
18	2.101
19	2.093
20 21 22 23	2.086 2.080 2.074 2.069 2.064
25	2.060
26	2.056
27	2.052
28	2.048
29	2.045

95th percent confidence interval value = 11.5 + 2.262 x  $(2.9/\sqrt{10})$  = 13.6 ppm

Thus, if the concentration of compound A in the waste-derived residue is below 13.6 ppm, then the waste-derived residue is eligible for the Bevill exemption for toxic compound A.

## 7.3 Normal Distribution Assumption

As noted in Section 7.2 above, this statistical approach (use of the 95th percent confidence interval about the mean) for calculation of the concentration in normal residue is based on the assumption that the concentration data are distributed normally. The Agency is aware that concentration data of this type may not be distributed normally, particularly when concentrations are near the detection limits. There are a number of procedures that can be used to test the distribution of a data set. For example, the Shapiro-Wilk test, examination of a histogram or plot of the data on normal probability paper, and examination of the coefficient of skewness are methods that may be applicable, depending on the nature of the data (Reference 1 and 2).

If the concentration data are not adequately represented by a normal distribution, the data may be transformed to attain a near normal distribution. The Agency has found that concentration data, especially when near detection levels, often exhibit a lognormal distribution. The assumption of a lognormal distribution has been used in various programs at EPA, such as in the Office of Solid Waste Land Disposal Restrictions program for determination of BDAT treatment standards. The transformed data may be tested for normality using the procedures identified above. If the transformed data are better represented by a normal distribution than the untransformed data, the transformed data should be used in determining the 95th percent confidence interval using the procedures in Section 7.2 above.

In all cases where the applicant for the Bevill exemption wishes to use other than an assumption of normally distributed data, or believes that use of an alternate statistical approach is appropriate to the specific data

set, the applicant must provide supporting rationale and demonstrate to the Director or permitting authority that the data treatment is based upon sound statistical practice.

# 7.4 Nondetect Values

The Agency is developing guidance regarding the treatment of nondetect values (data where the concentration of the constituent being measured is below the lowest concentration for which the analytical method is valid) in carrying out the statistical determinations described above. Until the guidance information is available, facilities may present their own approach to the handling of nondetect data points, but must provide supporting rationale in the operating record for consideration by the Director or permitting authority.

# 7.5 References

- 1. Shapiro, S,S. and Wilk, M.B. (1965), "An Analysis of Variance Test for Normality (complete samples), " Biometrika, 52, 591-611.
- 2. Bhattacharyya, G.K. and R.A. Johnson (1977), Statistical Concepts and Methods, John Wiley and Sons, New York.

# PROCEDURES FOR DETERMINING DEFAULT VALUES FOR AIR POLLUTION CONTROL SYSTEM REMOVAL EFFICIENCIES

During interim status, owners or operators of boilers and industrial furnaces burning hazardous waste must submit documentation to EPA that certifies that emissions of HCl, Cl<sub>2</sub>, metals, and particulate matter (PM) are not likely to exceed allowable emission rates. See certification of precompliance under 40 CFR 266.103(b). This documentation also establishes interim status feed rate and operating limits for the facility. For the initial certification, estimates of emissions and system removal efficiencies (SREs) can be made to establish the operating limits. Subsequently, owners or operators must use emissions testing to demonstrate that emissions do not exceed allowable levels, and to establish operating limits. See 40 CFR 266.103(c). However, initial estimates of emissions for certification of precompliance can be based on estimated or established SREs.

The SRE combines the effect of partitioning of the chorine, metals, or PM and the air pollution control system removal efficiency (APCS RE) for these pollutants. The SRE is defined as:

SRE = (species input - species emitted) / species input

The SRE can be calculated from the partitioning factor (PF) and APCS RE by the following formula:

SRE = 1 - [(PF/100) X (1 - APCS RE/100)]

where: PF - percentage of the pollutant partitioned to the combustion gas

Estimates of the PF and/or the APCS RE can be based on either EPA's default values or engineering judgement. EPA's default values for the APCS RE for metals, HCl, Cl<sub>2</sub>, and PM are described in this section. EPA's default values for partitioning of these pollutants are described in Section 9.0.

Guidelines for the use of engineering judgement to estimate APCS REs or PFs are described in Section 9.4.

## 8.1 APCS RE Default Values for Metals

EPA's default assumptions for APCS RE for metals are shown in Table 8.1-1. The default values in the table are conservative estimates of the removal efficiencies for metals in BIFs, depending on the volatility of the metal and the type of APCS.

The volatility of a metal depends on the temperature, the thermal input, the chlorine content of the waste, and the identity and concentration of the metal. Metals that do not vaporize at combustion zone temperatures are classified as "nonvolatile". Such metals typically enter the APCS in the form of large particles that are removed relatively easily. Metals that vaporize in the combustion zone and condense before entering the APCS are classified as "volatile". Such metals typically enter the APCS in the form of very fine, submicron particles that are rather inefficiently removed in many APCSs. Metals that vaporize in the combustion zone and do not condense before entering the APCS are classified as "very volatile". Such metals enter the APCS in the form of a vapor that is very inefficiently removed in many APCSs.

Typically, BIFs have combustion zone temperatures high enough to vaporize any hazardous metal at concentrations sufficient to exceed risk-based emission limits. For this reason, the default assumption is that there are no nonvolatile metals. Tables 8.1-2 and 8.1-3 are used to determine whether metals are classified as "volatile" or "very volatile" depending on the temperature entering the APCS, the thermal input, and whether the waste is chlorinated or nonchlorinated.

A waste is considered chlorinated if chlorine is present in concentrations greater than 0.1 percent by weight. In the EPA guidance document "Guidance for Metals and Hydrogen Chloride Controls for Hazardous Waste Incinerators, Volume IV of the Hazardous Waste Incineration Guidance Series," 1

Table 8.1-1

AIR POLLUTION CONTROL SYSTEMS (APCS) AND THEIR CONSERVATIVELY ESTIMATED EFFICIENCIES FOR CONTROLLING TOXIC METALS (%)

	Mo	Metal Volatility				
APCS	Nonvolatile	Volatile	Very Volatile			
WS	40	30	20			
VS-20	, 80	75	20			
VS-60	87	75	40			
ESP-1	90	75	0			
ESP-2	92	80	0			
ESP-4	95	80	0			
WESP	90	85	40			
FF	90	80	0			
SD/FF	97	90	0			
DS/FF	95	90	0			
IWS	90	87	75			

WS - Wet Scrubber including: Sieve Tray Tower Packed Tower Bubble Cap Tower

VS-20 - Venturi Scrubber, ca. 20-30 in W.G. \*p

VS-60 - Venturi Scrubber, ca. >60 in W.G. \*p

ESP-1 - Electrostatic Precipitator; 1 stage

ESP-2 - Electrostatic Precipitator; 2 stage

ESP-4 - Electrostatic Precipitator; 4 stage

IWS - Ionizing Wet Scrubber

DS - Dry Scrubber

FF - Fabric Filter (Baghouse)

SD - Spray Dryer (Wet/Dry Scrubber)

WESP - Wet Electrostatic Precipitator

Table 8.1-2

TEMPERATURE (F) ENTERING APCS ABOVE WHICH METALS ARE CLASSIFIED AS VERY VOLATILE IN COMBUSTION OF NONCHLORINATED WASTES

Metal		Thermal Input (MMBtu/hr) <sup>1</sup>				
Name	Symbol	1	10	100	1000	10000
Arsenic	As	320	280	240	200	160
Cadmium	Cd	1040	940	860	780	720
Chromium	Cr	2000	1760	1580	1420	1380
Beryllium	Be	1680	1440	1240	1080	980 !
Antimony	Sb	680	600	540	480	420
Barium	Ва	2240	1820	1540	1360	1240
Lead	Pb	1280	1180	_ 1080	1000	920
Mercury	Hg	340	300	260	220	180
Silver	Ag	1820	1640	1480	1340	1220.
Thallium	Tl	900	800	700	620	540

Interpolation of thermal input is not allowed. If a BIF fires between two ranges, the APCS temperature under the higher thermal input must be used.

Example: For a BIF firing 10 - 100 MMBtu/hr, Mercury is considered very volatile at APCS temperatures above 260 F and volatile at APCS temperatures of 260 F and below.

Table 8.1-3

TEMPERATURE (F) ENTERING APCS ABOVE WHICH METALS ARE CLASSIFIED AS VERY VOLATILE IN COMBUSTION OF CHLORINATED WASTES

Metal		Thermal Input (MMBtu/hr)1				
Name	Symbol	1	10	100	1000	10000
Arsenic	As	320	280	240	200	160
Cadmium	Cd	1040	940	. 860	780	720
Chromium	Cr	>140	>140	>140	>140	>140
Beryllium	Be	1680	1440	1240	1080	980
Antimony	Sb	680	600	540	480	420
Barium	Ba	2060	1840	1680	1540	1420
Lead	РЬ	>140	>140	>140	>140	>140
Mercury	Hg	340	300	260	220	180
Silver	Ag	1080	940	840	740	660
Thallium	Tl	900	800	700	620	540

Interpolation of thermal input is not allowed. If a BIF fires between two ranges, the APCS temperature under the higher thermal input must be used.

Example: For a BIF firing 10 - 100 MMBtu/hr, Mercury is considered very volatile at APCS temperatures above 260 F and volatile at APCS temperatures of 260 F and below.

1

one percent is used for the chlorinated/nonchlorinated cutoff. However, best engineering judgement, based on examination of pilot-scale data reported by Carroll et al.<sup>2</sup> on the effects of waste chlorine content on metals emissions, suggests that the 1 percent cutoff may not be sufficiently conservative.

Tables 8.1-2 and 8.1-3 were compiled based on equilibrium calculations. Metals are classified as very volatile at all temperatures above the temperature at which the vapor pressure of the metal is greater than 10 percent of the vapor pressure that results in emissions exceeding the most conservative risk-based emissions limits.

# 8.2 APCS RE Default Values for HCl and Cl<sub>2</sub>

Default assumptions for APCS RE for HCl in BIFs are shown in Table 8.2-1. This table is identical to the column for other BIFs except that cement kilns have a minimum HCl removal efficiency of 83 percent. Because of the alkaline nature of the raw materials in cement kilns, most of the chlorine is converted to chloride salts. Thus, the minimum APCS RE for HCl for cement kilns is independent of the APCS train.

Removal efficiency of  $\operatorname{Cl}_2$  for most types of APCS is generally minimal. Therefore, the default assumption for APCS RE for  $\operatorname{Cl}_2$  for all APCSs is 0 percent. This is applicable to all BIFs, including cement kilns.

# 8.3 APCS RE Default Values for Ash

Default assumptions for APCS RE for PM are also shown in Table 8.1-4. These figures are conservative estimates of PM removal efficiencies for different types of APCSs. They are identical to the figures in the Nonvolatile APCS RE column for hazardous metals presented in Table 8.1-1 because the same collection mechanisms and collection efficiencies that apply to nonvolatile metals also apply to PM.

Table 8.2-1

# AIR POLLUTION CONTROL SYSTEMS (APCS) AND THEIR CONSERVATIVELY ESTIMATED EFFICIENCIES FOR REMOVING HYDROGEN CHLORIDE (HC1) AND PARTICULATE MATTER (PM) (%)

		н	-	
A	PCD	Cement Kilns	Other BIFs	PM
ws		97	97	40
VS-20		97	97	80
VS-60		98	98	87
ESP-1		83	0	90
ESP-2		83	0	92
ESP-4		83	0	95
WESP		83	70	90
FF		83	0	90
SD/FF		98	98	97
DS/FF		98	98	95
WS/IWS		99	99	95
IWS		99	99	90

WS - Wet Scrubber including: Sieve Tray Tower
Packed Tower
Bubble Cap Tower

# PS - Proprietary Wet Scrubber Design

(A number of proprietary wet scrubbers have come on the market in recent years that are highly efficient on both partculates and corrosive gases. Two such units are offered by Calvert Environmental Equipment Co. and by Hydro-Sonic Systems, Inc.).

VS-20 - Venturi Scrubber, ca. 20-30 in W.G. ap

VS-60 - Venturi Scrubber, ca. >60 in W.G. ap

ESP-1 - Electrostatic Precipitator; 1 stage

ESP-2 - Electrostatic Precipitator; 2 stage

ESP-4 - Electrostatic Precipitator; 4 stage .

IWS - Ionizing Wet Scrubber

DS - Dry Scrubber

FF - Febric Filter (Baghouse)

SD - Spray Dryer (Wet/Dry Scrubber)

# 8.4 References

- 1. U.S. Environmental Protection Agency. "Guidance on Metals and Hydrogen Chloride Controls for Hazardous Waste Incinerators," Office of Solid Waste, Washington, D.C., August 1989.
- 2. Carroll, G.J., R.C. Thurnau, R.E. Maurnighan, L.R. Waterland, J.W. Lee, and D.J. Fournier. The Partitioning of Metals in Rotary Kiln Incineration. Proceedings of the Third International Conference on New Frontiers for Hazardous Waste Management. NTIS Document No. EPA/600/9-89/072, p. 555 (1989).

# PROCEDURES FOR DETERMINING DEFAULT VALUES FOR PARTITIONING OF METALS. ASH. AND TOTAL CHLORIDE/CHLORINE

Pollutant partitioning factor estimates can come from two sources: default assumptions or engineering judgement. EPA's default assumptions are discussed below for metals, HCl,  $Cl_2$ , and PM. The default assumptions are used to conservatively predict the partitioning factor for several types of BIFs. Engineering judgement-based partitioning factor estimates are discussed in Section 9.4.

# 9.1 Partitioning Default Value for Metals

To be conservative, the Agency is assuming that 100 percent of each metal in each feed stream is partitioned to the combustion gas. Owners/operators may use this default value or a supportable, site-specific value developed following the general guidelines provided in Section 9.4.

# 9.2 Special Procedures for Chlorine, HCl. and Cl.

The Agency has established the special procedures presented below for chlorine because the emission limits are based on the pollutants HC1 and C1<sub>2</sub> formed from chlorine fed to the combustor. Therefore, the owner/operator must estimate the controlled emission rate of both HCl and C1<sub>2</sub> and show that they do not exceed allowable levels.

- 1. The default partitioning value for the fraction of chlorine in the total feed streams that is partitioned to combustion gas is 100 percent. Owners/operators may use this default value or a supportable, site-specific value developed following the general guidelines provided in Section 9.4.
- 2. To determine the partitioning of chlorine in the combustion gas to HCl versus Cl<sub>2</sub>, either use the default values below or use supportable site-specific values developed following the general guidelines provided in Section 9.4.

- For BIFs excluding halogen acid furnaces (HAFs), with a total feed stream chlorine/hydrogen ratio ≤ 0.95, the default partitioning factor is 20 percent Cl<sub>2</sub>, 80 percent HCl.
- For HAFs and for BIFs with a total feed stream chlorine/hydrogen ratio > 0.95, the default partitioning factor is 100 percent Cl<sub>2</sub>.
- 3. To determine the uncontrolled (i.e., prior to acid gas APCS) emission rate of HCl and  $\text{Cl}_2$ , multiply the feed rate of chlorine times the partitioning factor for each pollutant. Then, for HCl, convert the chorine emission rate to HCl by multiplying it by the ratio of the molecular weight of Cl to the molecular weight of HCl (i.e., 35.5/36.5). No conversion is needed for  $\text{Cl}_2$ .

# 9.3 Special Procedures for Ash

This section: (1) explains why ash feed rate limits are not applicable to cement and light-weight aggregate kilns; (2) presents the default partitioning values for ash; and (3) explains how to convert the 0.08 gr/dscf, corrected to  $7 \ 0_2$ , PM emission limit to a PM emission rate.

Waiver for Cement and Light-Weight Aggregate Kilns. For cement kilns and light-weight aggregate kilns, raw material feed streams contain the vast majority of the ash input, and a significant amount of the ash in the feed stream is entrained into the kiln exhaust gas. For these devices, the ash content of the hazardous waste stream is expected to have a negligible effect on total ash emissions. For this reason, there is no ash feed rate compliance limit for cement kilns or light-weight aggregate kilns. Nonetheless, cement kilns and light-weight aggregate kilns are required to initially certify that PM emissions are not likely to exceed the PM limit, and subsequently, certify through compliance testing that the PM limit is not exceeded.

<u>Default Partitioning Value for Ash</u>. The default assumption for partitioning of ash depends on the feed stream firing system. There are two methods by which materials may be fired into BIFs: suspension-firing and bed-firing.

The suspension category includes atomized and lanced pumpable liquids and suspension-fired pulverized solids. The default partitioning assumption for materials fired by these systems is that 100 percent of the ash partitions to the combustion gas.

The bed-fired category consists principally of stoker boilers and raw materials (and in some cases containerized hazardous waste) fed into cement and light-weight aggregate kilns. The default partitioning assumption for materials fired on a bed is that 5 percent of the ash partitions to the combustion gas.

Converting the PM Concentration-Based Standard to a PM Mass Emission Rate. The emission limit for BIFs is 0.08 gr/dscf, corrected to  $7 \% 0_2$ , unless a more stringent standard applies [e.g., a New Source Performance Standard (NSPS) or a State standard implemented under the State Implementation Plan (SIP)]. To convert the 0.08 gr/dscf standard to a PM mass emission rate:

- 1. Determine the flue gas  $0_2$  concentration (percent by volume, dry) and flue gas flow rate (dry standard cubic feet per minute); and
- 2. Calculate the allowable PM mass emission rate by multiplying the concentration-based PM emission standard times the flue gas flow rate times a dilution correction factor equal to  $[(21 0_2 \text{ concentration from step 1})/(21 7)]$ .

# 9.4 <u>Use of Engineering Judgement to Estimate Partitioning and APCS RE Values</u>

Engineering judgement may be used in place of EPA's conservative default assumptions to estimate partitioning and APCS RE values provided that the engineering judgement is defensible and properly documented. To properly document engineering judgement, the owner/operator must keep a written record of all assumptions and calculations necessary to justify the APCS RE used. The owner/operator must provide this record to the Director upon request and must be prepared to defend the assumptions and calculations used.

If the engineering judgement is based on emissions testing, the testing will often document the emission rate of a pollutant relative to the feed rate of that pollutant rather than the partitioning factor or APCS RE.

Examples of situations where the use of engineering judgement may be supportable to estimate a partitioning factor, APCS RE, or SRE include:

- Using emissions testing data from the facility to support an SRE, even though the testing may not meet full QA/QC procedures (e.g., triplicate test runs). The closer the test results conform with full QA/QC procedures and the closer the operating conditions during the test conform with the established operating conditions for the facility, the more supportable the engineering judgement will be.
- Applying emissions testing data documenting an SRE for one metal, including nonhazardous surrogate metals to another less volatile metal.
- Applying emissions testing data documenting an SRE from one facility to a similar facility.
- Using APCS vendor guarantees of removal efficiency.

# 9.5 Restrictions on Use of Test Data

The measurement of an SRE or an APCS RE may be limited by the detection limits of the measurement technique. If the emission of a pollutant is undetectable, then the calculation of SRE or APCS RE should be based on the lower limit of detectability. An SRE or APCS RE of 100 percent is not acceptable.

Further, mass balance data of facility inputs, emissions, and products/residues may not be used to support a partitioning factor, given the inherent uncertainties of such procedures. Partitioning factors other than the default values may be supported based on engineering judgement, considering, for example, process chemistry. Emissions test data may be used to support an engineering judgement-based SRE, which includes both partitioning and APCS RE.

### Section 10.0

# ALTERNATIVE METHODOLOGY FOR IMPLEMENTING METALS CONTROLS

### 10.1 Applicability

This method for controlling metals emissions applies to cement kilns and other industrial furnaces operating under interim status that recycle emission control residue back into the furnace.

# 10.2 Introduction

Under this method, cement kilns and other industrial furnaces that recycle emission control residue back into the furnace must comply with a kiln dust concentration limit (i.e., a collected particulate matter (PM) limit) for each metal, as well as limits on the maximum feedrates of each of the metals in: (1) pumpable hazardous waste; and (2) all hazardous waste.

The following subsections describe how this method for controlling metals emissions is to be implemented:

- Subsection 10.3 discusses the basis of the method and the assumptions upon which it is founded;
- Subsection 10.4 provides an overview of the implementation of the method;
- Subsection 10.5 is a step-by-step procedure for implementation of the method;
- Subsection 10.6 describes the compliance procedures for this method; and
- Appendix A describes the statistical calculations and tests to be used in the method.

# 10.3 Basis

The viability of this method depends on three fundamental assumptions:

- (1) Variations in the ratio of the metal concentration in the emitted particulate to the metal concentration in the collected kiln dust (referred to as the enrichment factor or EF) for any given metal at any given facility will fall within a normal distribution that can be experimentally determined.
- (2) The metal concentrations in the collected kiln dust can be accurately and representatively measured (using procedures specified in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (SW-846), incorporated by reference in 40 CFR 260.11).
- (3) The facility will remain in compliance with the applicable particulate matter (PM) emission standard.

Given these assumptions, metal emissions can be related to the measured concentrations in the collected kiln dust by the following equation:

$$ME\left(\frac{1b \ Emitted \ Metal}{hr}\right) =$$

$$PME\left(\frac{1b \ PM}{hr}\right) DMC\left(\frac{1b \ Dust \ Metal}{1b \ Dust}\right) EF\left(\frac{1b \ Emitted \ Metal/1b \ PM}{1b \ Dust \ Metal/1b \ Dust}\right) \tag{1}$$

Where:

ME is the metal emitted;

PME is the particulate matter emitted;

DMC is the metal concentration in the collected kiln dust; and EF is the enrichment factor, which is the ratio of the metal concentration in the emitted particulate matter to the metal concentration in the collected kiln dust.

This equation can be rearranged to calculate a maximum allowable dust metal concentration limit (DMCL) by assuming worst-case conditions that: metal emissions are at the Tier III (or Tier II) limit (see 40 CFR 266.106), and that particulate emissions are at the particulate matter limit (PML):

$$DMCL\left(\frac{\text{1b Dust Metal}}{\text{1b Dust}}\right) = \frac{\text{Tier III Limit}\left(\frac{\text{1b Emitted Metal}}{\text{hr}}\right)}{PML\left(\frac{\text{1b PM}}{\text{hr}}\right) EF\left(\frac{\text{1b Emitted Metal/1b PM}}{\text{1b Dust Metal/1b Dust}}\right)}$$
(2)

The enrichment factor used in the above equation must be determined experimentally from a minimum of 10 tests in which metal concentrations are measured in kiln dust and stack samples taken simultaneously. This approach provides a range of enrichment factors that can be inserted into a statistical distribution (t-distribution) to determine  $EF_{952}$  and  $EF_{992}$ .  $EF_{952}$  is the value at which there is a 95% confidence level that the enrichment factor is below this value at any given time. Similarly,  $EF_{992}$  is the value at which there is a 99% confidence level that the enrichment factor is below this value at any given time.  $EF_{952}$  is used to calculate the "violation" dust metal concentration limit (DMCL<sub>v</sub>):

$$DMCL_{v}\left(\frac{1b \ Dust \ Metal}{1b \ Dust}\right) = \frac{Tier \ III \ Limit\left(\frac{1b \ Emitted \ Metal}{hr}\right)}{PML\left(\frac{1b \ PM}{hr}\right) \ EF_{950}\left(\frac{1b \ Emitted \ Metal/1b \ PM}{1b \ Dust \ Metal/1b \ Dust}\right)}$$
(3)

If the kiln dust metal concentration is just above this "violation" limit, and the PM emissions are at the PM emissions limit, there is a 5% chance that the metal emissions are above the Tier III limit. In such a case, the facility would be in violation of the metals standard.

To provide a margin of safety, a second, more conservative kiln dust metal concentration limit is also used. This "conservative" dust metal concentration limit (DMCL<sub>c</sub>) is calculated using a "safe" enrichment factor

(SEF). If  $EF_{992}$  is greater than two times the value of  $EF_{952}$ , the "safe" enrichment factor can be calculated using Equation 4a:

$$SEF \ge 2 EF_{958}$$
 (4a)

If  $EF_{992}$  is not greater than two times the value of  $EF_{952}$ , the "safe" enrichment factor can be calculated using Equation 4b:

$$SEF \ge EF_{998}$$
 (4b)

In cases where the enrichment factor cannot be determined because the kiln dust metal concentration is nondetectable, the "safe" enrichment factor is as follows:

$$SEF = 100 \tag{4c}$$

For all cases, the "conservative" dust metal concentration limit is calculated using the following equation:

$$DMCL_{c}\left(\frac{1b \ Dust \ Metal}{1b \ Dust}\right) = \frac{Tier \ III \ Limit\left(\frac{1b \ Emitted \ Metal}{hr}\right)}{PML\left(\frac{1b \ PM}{hr}\right) \ SEF\left(\frac{1b \ Emitted \ Metal/1b \ PM}{1b \ Dust \ Metal/1b \ Dust}\right)}$$
(5)

If the kiln dust metal concentration at a facility is just above the "conservative" limit based on the "safe" enrichment factor provided in Equation 4a, and the PM emissions are at the PM emissions limit, there is a 5% chance that the metal emissions are above one-half the Tier III limit. If the kiln dust metal concentration at the facility is just above the "conservative" limit based on the "safe" enrichment factor provided in Equation 4b, and the PM emissions are at the PM emissions limit, there is a 1% chance that the metal emissions are above the Tier III limit. In either case, the facility

would be unacceptably close to a violation. If this situation occurs more than 5% of the time, the facility would be required to rerun the series of 10 tests to determine the enrichment factor. To avoid this expense, the facility would be advised to reduce its metals feedrates or to take other appropriate measures to maintain its kiln dust metal concentrations in compliance with the "conservative" dust metal concentration limits.

In cases where the enrichment factor cannot be determined because the kiln dust metal concentration is nondetectable, and thus no  $EF_{95Z}$  exists, the "violation" dust metal concentration limit is set at ten times the "conservative" limit:

$$DMCL_{v} = 10 \times DMCL_{c} \tag{6}$$

# 10.4 Overview

The flowchart for implementing the method is shown in Figure 10.4-1. The general procedure is as follows:

- Follow the certification of precompliance procedures described in Subsection 10.6 (to comply with 40 CFR 266.103(b)).
- For each metal of concern, perform a series of tests to establish the relationship (enrichment factor) between the concentration of emitted metal and the metal concentration in the collected kiln dust.
- Use the demonstrated enrichment factor, in combination with the Tier III (or Tier II) metal emission limit and the most stringent applicable particulate emission limit, to calculate the "violation" and "conservative" dust metal concentration limits. Include this information with the certification of compliance under 40 CFR 266.103(c).

ify Limit Exceeded

#### Compliance Implementation Flow Chart Tier III **Emission Limit Precompliance** Test Plan - See Figure 2 Waste Analysis Plan Tests to Determine Fail Statistical Test to Time Available **Enrichment Factor** Emissions Determine if Enrichment Before Certification of -3 out of 1st 5 tests at Factor Has Increased Compliance is Due? compliance limits L-No Increased Notify Director. Pass Emissions Yes Us to 720 Waste-Obtain Time **Burning Hours** Allowed to Submit Extension or May Retest Revised Cartification Stop Burning Food Rate Limits Reduced by 50% for Metal in Violatian Certification Not Increased -Set "Conservative" and Quarterly "Violation" Klin Dust Violation of Yes Concentration Limits Enrichment IS Standards Factor More Than 3 **Verification** Failures in Lost Tests Yes 60 Tests? **Exceed Violation Kiln Dust Concentration** Now Pass Daily and/or Weekly Kiin Limit? Dust Monitoring for Quarterly Test Continued Compliance Yes -Due? Still Exceed Optional Analysis of Spare **Exceed Conservative** Samples to Statistically No · Kiln Dust Concentration?

- Perform daily and/or weekly monitoring of the cement kiln dust metal concentration to ensure (with appropriate QA/QC) that the metal concentration does not exceed either limit.
  - If the cement kiln dust metal concentration exceeds the "conservative" limit more than 5% of the time (i.e., more than three failures in last 60 tests), the series of tests to determine the enrichment factor must be repeated.
  - If the cement kiln dust metal concentration exceeds the "violation" limit, a violation has occurred.
- Perform quarterly tests to verify that the enrichment factor has not increased significantly. If the enrichment factor has increased, the series of tests to determine the enrichment factor must be repeated.

# 10.5 Implementation Procedures

A step-by-step description for implementing the method is provided below:

- (1) Prepare initial limits and test plans.
  - Determine the Tier III metal emission limit. The Tier II metal emission limit may also be used (see 40 CFR 266.106).
  - Determine the applicable PM emission standard. This standard is the most stringent particulate emission standard that applies to the facility. A facility may elect to restrict itself to an even more stringent self-imposed PM emission standard, particularly if the facility finds that it is easier to control particulate emissions than to reduce the kiln dust concentration of a certain metal (i.e., lead).

- Determine which metals need to be monitored (i.e., all hazardous metals for which Tier III emission limits are lower than PM emission limits -- assuming PM is pure metal).
- Follow the compliance procedures described in Subsection 10.6.
- Follow the guidelines described in SW-846 for preparing test plans and waste analysis plans for the following tests:
  - Compliance tests to determine limits on metal feedrates in pumpable hazardous wastes and in all hazardous wastes (as well as to determine other compliance parameters);
  - Initial tests to determine enrichment factors;
  - Quarterly tests to verify enrichment factors;
  - Analysis of hazardous waste feedstreams; and
  - Daily and/or weekly monitoring of kiln dust for continuing compliance.
- (2) Conduct tests to determine the enrichment factor.
  - These tests must be conducted within a 14-day period. No more than two tests may be conducted in any single day. If the tests are not completed within a 14-day period, they must be repeated.
  - Simultaneous stack samples and kiln dust samples must be taken.
    - Stack sampling must be conducted with the multiple metals train according to procedures provided in Section 10.3 of this Methods Manual.
    - Kiln dust sampling must be conducted as follows:
      - -- Follow the sampling and analytical procedures described in SW-846 and the waste analysis plan as they pertain to the condition and accessibility of the dust.
      - -- Samples should be representative of the last ESP or Fabric Filter in the APCS series.

- The feedrates of hazardous metals in all pumpable hazardous waste streams and in all hazardous waste streams must be monitored during these tests. It is recommended (but not required) that the feedrates of hazardous metals in all feedstreams also be monitored.
- At least ten single (noncomposited) runs are required during the tests.
  - The facility must follow a normal schedule of kiln dust recharging for all of the tests.
  - Three of the first five tests must be compliance tests in conformance with 40 CFR 266.103(c); i.e., they must be used to determine maximum allowable feedrates of metals in pumpable hazardous wastes, and in all hazardous wastes, as well as to determine other compliance limits (see 40 CFR 266.103(c)(1)).
  - The remainder of the tests need not be conducted under full compliance test conditions; however, the facility must operate at its compliance test production rate, and it must burn hazardous waste during these tests such that the feedrate of each metal for pumpable and total hazardous wastes is at least 25% of the feedrate during compliance testing. If these criteria, and those discussed below, are not met for any parameter during a test, then either the test is not valid for determining enrichment factors under this method, or the compliance limits for that parameter must be established based on these test conditions rather than on the compliance test conditions.
- Verify that compliance emission limits are not exceeded.
  - Metal emissions must not exceed Tier III (or Tier II) limits.
  - PM emissions must not exceed the most stringent of applicable PM standards (or an optional self-imposed particulate standard).

- The facility must generate normal, marketable product using normal raw materials and fuels under normal operating conditions (for parameters other than those specified under this method) when these tests are conducted.
- Chromium must be treated as a special case:
  - The enrichment factor for total chromium is calculated in the same way as the enrichment factor for other metals (i.e., the enrichment factor is the ratio of the concentration of total chromium in the emitted particulate matter to the concentration of total chromium in the collected kiln dust).
  - The enrichment factor for hexavalent chromium (if measured) is defined as the ratio of the concentration of hexavalent chromium in the emitted particulate matter to the concentration of total chromium in the collected kiln dust.
- (3) Use the enrichment factors measured in Step 2 to determine  $EF_{95Z}$ ,  $EF_{99Z}$ , and SEF.
  - Calculate EF<sub>952</sub> and EF<sub>992</sub> according to the t-distribution as described in Appendix A.
  - Calculate SEF by
    - Equation 4a if  $EF_{952}$  is determinable and if  $EF_{992}$  is greater than two times  $EF_{952}$ ,
    - Equation 4b if  $EF_{95Z}$  is determinable and if  $EF_{99Z}$  is not greater than two times  $EF_{95Z}$ .
    - Equation 4c if EF<sub>951</sub> is not determinable.

The facility may choose to set an even more conservative SEF to give itself a larger margin of safety between the point where corrective action is necessary and the point where a violation occurs.

- (4) Prepare certification of compliance
  - Calculate the "conservative" dust metal concentration limit (DMCL<sub>e</sub>) using Equation 5.
    - Chromium is treated as a special case. The "conservative" kiln dust chromium concentration limit is set for total chromium, not for hexavalent chromium. The limit for total chromium must be calculated using the Tier III (or Tier II) metal limit for hexavalent chromium.
      - -- If the stack samples described in Step 2 were analyzed for hexavalent chromium, the SEF based on the hexavalent chromium enrichment factors (as defined in Step 2) must be used in this calculation.
      - -- If the stack samples were not analyzed for hexavalent chromium, then the SEF based on the total chromium enrichment factor must be used in this calculation.
  - Calculate the "violation" dust metal concentration limit (DMCL $_{\rm v}$ ) using Equation 3 if EF $_{952}$  is determinable, or using Equation 6 if EF $_{952}$  is not determinable.
    - Chromium is treated as a special case. The "violation" kiln dust chromium concentration limit is set for total chromium, not for hexavalent chromium. The limit for total chromium must be calculated using the Tier III (or Tier II) metal limit for hexavalent chromium.
      - -- If the stack samples taken in Step 2 were analyzed for hexavalent chromium, the  $EF_{952}$  based on the hexavalent chromium enrichment factor (as defined in Step 2) should be used in this calculation.
      - -- If the stack samples were not analyzed for hexavalent chromium, the  $EF_{95Z}$  based on the total chromium enrichment factor must be used in this calculation.
  - Submit certification of compliance.

- Steps 2-4 must be repeated for recertification, which is required once every 3 years (see §266.103(d)).
- (5) Monitor metal concentrations in kiln dust for continuing compliance, and maintain compliance with all compliance limits for the duration of interim status.
  - Metals to be monitored during compliance testing are classified as either "critical" or "noncritical" metals.
    - All metals must initially be classified as "critical" metals and be monitored on a daily basis.
    - A "critical" metal may be reclassified as a "noncritical" metal if its concentration in the kiln dust remains below 10% of its "conservative" kiln dust metal concentration limit for 30 consecutive daily samples. "Noncritical" metals must be monitored on a weekly basis.
    - A "noncritical" metal must be reclassified as a "critical" metal if its concentration in the kiln dust is above 10% of its "conservative" kiln dust metal concentration limit for any single daily or weekly sample.
  - Noncompliance with the sampling and analysis schedule prescribed by this method is a violation of the metals controls under §266.103.
  - Follow the sampling, compositing, and analytical procedures described in this method and in SW-846 as they pertain to the condition and accessibility of the kiln dust.
  - Follow the same procedures and sample at the same locations as were used for kiln dust samples collected to determine the enrichment factors (as discussed in Step 2).
  - Samples must be collected at least once every 8 hours, and a daily composite must be prepared according to SW-846 procedures.

- At least one composite sample is required. This sample is referred to as the "required" sample.
- For QA/QC purposes, a facility may elect to collect two or more additional samples. These samples are referred to as the "spare" samples. These additional samples must be collected over the same time period and according to the same procedures as those used for the "required" sample.
- Samples for "critical" metals must be daily composites.
- Samples for "noncritical" metals must be weekly composites.

  These samples can be composites of the original 8-hour samples, or they can be composites of daily composite samples.
- Analyze the "required" sample to determine the concentration of each metal.
  - This analysis must be completed within 48 hours of the close of the sampling period. Failure to meet this schedule is a violation of the metals standards of §266.103.
- If the "conservative" kiln dust metal concentration limit is exceeded for any metal, refer to Step 8.
- If the "conservative" kiln dust metal concentration limit is not exceeded, continue with the daily or weekly monitoring (Step 5) for the duration of interim status.
- Conduct quarterly enrichment factor verification tests, as described in Step 6.
- (6) Conduct quarterly enrichment factor verification tests.
  - After certification of compliance with the metals standards, a facility must conduct quarterly enrichment factor verification tests every three months for the duration of interim status. The first quarterly test must be completed within three months of

certification (or recertification). Each subsequent quarterly test must be completed within three months of the preceding quarterly test. Failure to meet this schedule is a violation.

- Simultaneous stack samples and kiln dust samples must be collected.
- Follow the same procedures and sample at the same locations as were used for kiln dust samples and stack samples collected to determine the enrichment factors (as discussed in Step 2).
- At least three single (noncomposited) runs are required. These tests need not be conducted under the operating conditions of the initial compliance test; however, the facility must operate under the following conditions:
  - It must operate at compliance test production rate.
  - It must burn hazardous waste during the test, and for the 2-day period immediately preceding the test, such that the feedrate of each metal for pumpable and total hazardous wastes consist of at least 25% of the operating limits established during the compliance test.
  - It must remain in compliance with all compliance parameters (see §266.103(c)(1)).
  - It must follow a normal schedule of kiln dust recharging.
  - It must generate normal marketable product from normal raw materials during the tests.
- (7) Conduct a statistical test to determine if the enrichment factors measured in the quarterly verification tests have increased significantly from the enrichment factors determined in the tests conducted in Step 2. The enrichment factors have increased significantly if all three of the following criteria are met:
  - By applying the t-test described in Appendix A, it is determined that the enrichment factors measured in the quarterly tests are

not taken from the same population as the enrichment factors measured in the Step 2 tests;

- The  $EF_{95Z}$  calculated for the combined data sets (i.e., the quarterly test data and the original Step 2 test data) according to the t-distribution (described in Appendix A) is more than 10% higher than the  $EF_{95Z}$  based on the enrichment factors previously measured in Step 2; and
- The highest measured kiln dust metal concentration recorded in the previous quarter is more than 10% of the "violation" kiln dust concentration limit that would be calculated from the combined  $EF_{952}$ .

If the enrichment factors have increased significantly, the tests to determine the enrichment factors must be repeated (refer to Step 11). If the enrichment factors have not increased significantly, continue to use the kiln dust metal concentration limits based on the enrichment factors previously measured in Step 2, and continue with the daily and/or weekly monitoring described in Step 5.

- (8) If the "conservative" kiln dust metal concentration limit was exceeded for any metal in any single analysis of the "required" kiln dust sample, the "spare" samples corresponding to the same period may be analyzed to determine if the exceedance was due to a sampling or analysis error.
  - If no "spare" samples were taken, refer to Step 9.
  - If the average of all the samples for a given day (or week, as applicable) (including the "required" sample and the "spare" samples) does not exceed the "conservative" kiln dust metal concentration limit, no corrective measures are necessary; continue with the daily and/or weekly monitoring as described in Step 5.

- If the average of all the samples for a given day (or week, as applicable) exceeds the "conservative" kiln dust metal concentration limit, but the average of the "spare" samples is below the "conservative" kiln dust metal concentration limit, apply the Q-test, described in Appendix A, to determine whether the "required" sample concentration can be judged as an outlier.
  - If the "required" sample concentration is judged an outlier, no corrective measures are necessary; continue with the daily and/or weekly monitoring described in Step 5.
  - If the "required" sample concentration is not judged an outlier, refer to Step 9.
- (9) Determine if the "violation" kiln dust metal concentration has been exceeded based on either the average of all the samples collected during the 24-hour period in question, or if discarding an outlier can be statistically justified by the Q-test described in Appendix A, on the average of the remaining samples.
  - exceeded, a violation with dust metal concentration limit has been exceeded, a violation of the metals controls under \$266.103(c) has occurred. Notify the Director that a violation has occurred. Hazardous waste may be burned for testing purposes for up to 720 operating hours to support a revised certification of compliance. Note that the Director may grant an extension of the hours of hazardous waste burning under \$266.103(c)(7) if additional burning time is needed to support a revised certification for reasons beyond the control of the owner or operator. Until a revised certification of compliance is submitted to the Director, the feedrate of the metals in violation in total and pumpable hazardous waste feeds is limited to 50% of the previous compliance test limits.

- If the "violation" kiln dust metal concentration has not been exceeded:
  - If the exceedance occurred in a daily composite sample, refer to Step 10.
  - If the exceedance occurred in a weekly composite sample, refer to Step 11.
- (10) Determine if the "conservative" kiln dust metal concentration limit has been exceeded more than three times in the last 60 days.
  - If not, log this exceedance and continue with the daily and/or weekly monitoring (Step 5).
  - If so, the tests to determine the enrichment factors must be repeated (refer to Step 11).
  - This determination is made separately for each metal; For example,
    - Three exceedances for each of the ten hazardous metals are allowed within any 60-day period.
    - Four exceedances of any single metal in any 60-day period is not allowed.
  - This determination should be made daily, beginning on the first day of daily monitoring. For example, if four exceedances of any single metal occur in the first four days of daily monitoring, do not wait until the end of the 60-day period; refer immediately to Step 11.
- (11) The tests to determine the enrichment factor must be repeated if: (1) more than three exceedances of the "conservative" kiln dust metal concentration limit occur within any 60 consecutive daily samples; (2) an excursion of the "conservative" kiln dust metal concentration limit occurs in any weekly sample; or (3) a quarterly test indicates that the enrichment factors have increased significantly.

- The facility must notify the Director if these tests must be repeated.
- The facility has up to 720 hazardous-waste-burning hours to redetermine the enrichment factors for the metal or metals in question and to recertify (beginning with a return to Step 2). During this period, the facility must reduce the feed rate of the metal in violation by 50%. If the facility has not completed the recertification process within this period, it must stop burning or obtain an extension. Hazardous waste burning may resume only when the recertification process (ending with Step 4) has been completed.
- Meanwhile, the facility must continue with daily kiln dust metals monitoring (Step 5) and must remain in compliance with the "violation" kiln dust metal concentration limits (Step 9).

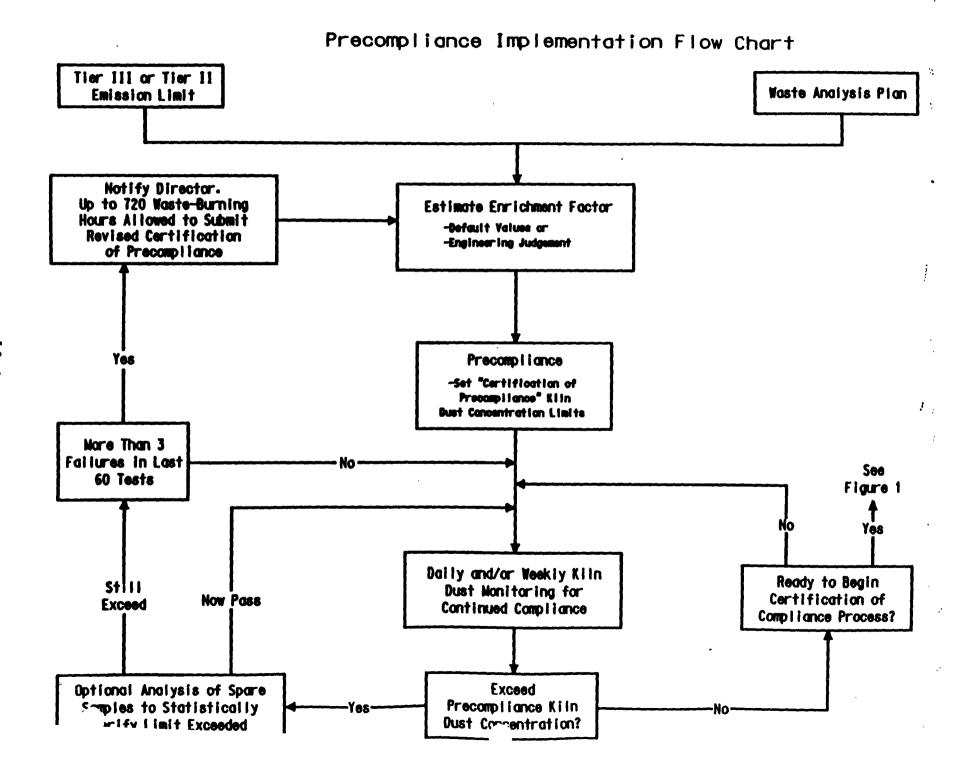
#### 10.6 Precompliance Procedures

Cement kilns and other industrial furnaces that recycle emission control residue back into the furnace must comply with the same certification schedules and procedures (with the few exceptions described below) that apply to other boilers and industrial furnaces. These schedules and procedures, as set forth in §266.103, require no later than the effective date of the rule, each facility submit a certification which establishes precompliance limits for a number of compliance parameters (see §266.103(b)(3)), and that each facility immediately begin to operate under these limits.

These precompliance limits must ensure that interim status emissions limits for hazardous metals, particulate matter, HCl, and  $\text{Cl}_2$  are not likely to be exceeded. Determination of the values of the precompliance limits must be made based on either (1) conservative default assumptions provided in this Methods Manual, or (2) engineering judgement.

The flowchart for implementing the precompliance procedures is shown in Figure 10.6-1. The step-by-step precompliance implementation procedure is described below. The precompliance implementation procedures and numbering scheme are similar to those used for the compliance procedures described in Subsection 10.5.

- (1) Prepare initial limits and test plans.
  - Determine the Tier III metal emission limit. The Tier II metal emission limit may also be used (see 40 CFR 266.106).
  - Determine the applicable PM emission standard. This standard is the most stringent particulate emission standard that applies to the facility. A facility may elect to restrict itself to an even more stringent self-imposed PM emission standard, particularly if the facility finds that it is easier to control particulate emissions than to reduce the kiln dust concentration of a certain metal (i.e., lead).
  - Determine which metals need to be monitored (i.e., all hazardous metals for which Tier III emission limits are lower than PM emission limits -- assuming PM is pure metal).
  - Follow the procedures described in SW-846 for preparing waste analysis plans for the following tasks:
    - Analysis of hazardous waste feedstreams.
    - Daily and/or weekly monitoring of kiln dust concentrations for continuing compliance.
- (2) Determine the "safe" enrichment factor for precompliance. In this context, the "safe" enrichment factor is a conservatively high estimate of the enrichment factor (the ratio of the emitted metal concentration to the metal concentration in the collected kiln dust). The "safe" enrichment factor must be calculated from either conservative default values, or engineering judgement.



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- Conservative default values for the "safe" enrichment factor are as follows:
  - SEF 10 for all hazardous metals except mercury. SEF 10 for antimony, arsenic, barium, beryllium, cadmium, chromium, lead, silver, and thallium.
  - SEF = 100 for mercury.
- Engineering judgement may be used in place of conservative default assumptions provided that the engineering judgement is defensible and properly documented. The facility must keep a written record of all assumptions and calculations necessary to justify the SEF. The facility must provide this record to EPA upon request and must be prepared to defend these assumptions and calculations.

  Examples of situations where the use of engineering judgement is appropriate include:
  - Use of data from precompliance tests;
  - Use of data from previous compliance tests; and
  - Use of data from similar facilities.
- (3) This step does not apply to precompliance procedures.
- (4) Prepare certification of precompliance.
  - Calculate the "conservative" dust metal concentration limit (DMCL<sub>e</sub>) using Equation 5.
  - Submit certification of precompliance. This certification must include precompliance limits for all compliance parameters that apply to other boilers and industrial furnaces (i.e., those that do not recycle emission control residue back into the furnace) as listed in \$266.103(b)(3), except that it is not necessary to set precompliance limits on maximum feedrate of each hazardous metal in all combined feedstreams.

- Furnaces that recycle collected PM back into the furnace (and that elect to comply with this method (see §266.103(c)(3)(ii)) are subject to a special precompliance parameter, however. They must establish precompliance limits on the maximum concentration of each hazardous metal in collected kiln dust. (which must be set according to the procedures described above).
- (5) Monitor metal concentration in kiln dust for continuing compliance, and maintain compliance with all precompliance limits until certification of compliance has been submitted.
  - Metals to be monitored during precompliance testing are classified as either "critical" or "noncritical" metals.
    - All metals must initially be classified as "critical" metals and be monitored on a daily basis.
    - A "critical" metal may be reclassified as a "noncritical" metal if its concentration in the kiln dust remains below 10% of its "conservative" kiln dust metal concentration limit for 30 consecutive daily samples. "Noncritical" metals must be monitored on a weekly basis, at a minimum.
    - A "noncritical" metal must be reclassified as a "critical" metal if its concentration in the kiln dust is above 10% of its "conservative" kiln dust metal concentration limit for any single daily or weekly sample.
  - It is a violation if the facility fails to analyze the kiln dust for any "critical" metal on any single day or for any "noncritical" metal during any single week, when hazardous waste is burned.
  - Follow the sampling, compositing, and analytical procedures described in this method and in SW-846 as they pertain to the condition and accessibility of the kiln dust.

- Samples must be collected at least once every 8 hours, and a daily composite prepared according to SW-846 procedures.
  - At least one composite sample is required. This sample is referred to as the "required" sample.
  - For QA/QC purposes, a facility may elect to collect two or more additional samples. These samples are referred to as the "spare" samples. These additional samples must be collected over the same time period and according to the same procedures as those used for the "required" sample.
  - Samples for "critical" metals must be daily composites.
  - Samples for "noncritical" metals must be weekly composites, at a minimum. These samples can be composites of the original 8-hour samples, or they can be composites of daily composite samples.
- Analyze the "required" sample to determine the concentration of each metal.
  - This analysis must be completed within 48 hours of the close of the sampling period. Failure to meet this schedule is a violation.
- If the "conservative" kiln dust metal concentration limit is exceeded for any metal, refer to Step 8.
- If the "conservative" kiln dust metal concentration limit is not exceeded, continue with the daily and/or weekly monitoring (Step 5) for the duration of interim status.
- (6) This step does not apply to precompliance procedures.
- (7) This step does not apply to precompliance procedures.
- (8) If the "conservative" kiln dust metal concentration limit was exceeded for any metal in any single analysis of the "required" kiln dust sample,

- the "spare" samples corresponding to the same period may be analyzed to determine if the exceedance is due to a sampling or analysis error.
- If no "spare" samples were taken, refer to Step 9.
- If the average of all the samples for a given day (or week, as applicable) (including the "required" sample and the "spare" samples) does not exceed the "conservative" kiln dust metal concentration limit, no corrective measures are necessary; continue with the daily and/or weekly monitoring as described in Step 5.
- If the average of all the samples for a given day (or week, as applicable) exceeds the "conservative" kiln dust metal concentration limit, but the average of the "spare" samples is below the "conservative" kiln dust metal concentration limit, apply the Q-test, described in Appendix A, to determine whether the "required" sample concentration can be judged as an outlier.
  - If the "required" sample concentration is judged an outlier, no corrective measures are necessary; continue with the daily and/or weekly monitoring described in Step 5.
  - If the "required" sample concentration is not judged an outlier, refer to Step 10.
- (9) This step does not apply to precompliance procedures.
- (10) Determine if the "conservative" kiln dust metal concentration limit has been exceeded more than three times in the last 60 days.
  - If not, log this exceedance and continue with the daily and/or weekly monitoring (Step 5).
  - If so, the tests to determine the enrichment factors must be repeated (refer to Step 11).

- This determination is made separately for each metal; for example
  - Three exceedances for each of the ten hazardous metals are allowed within any 60-day period.
  - Four exceedances of any single metal in any 60-day period is not allowed.
- This determination should be made daily, beginning on the first day of daily monitoring. For example, if four exceedances of any single metal occur in the first four days of daily monitoring, do not wait until the end of the 60-day period; refer immediately to Step 11.
- (11) A revised certification of precompliance must be submitted to the Director (or certification of compliance must be submitted) if: (1) more than three exceedances of the "conservative" kiln dust metal concentration limit occur within any 60 consecutive daily samples; or (2) an exceedance of the "conservative" kiln dust metal concentration limit occurs in any weekly sample.
  - The facility must notify the Director if a revised certification of precompliance must be submitted.
  - The facility has up to 720 waste-burning hours to submit a certification of compliance or a revised certification of precompliance. During this period, the feed rate of the metal in violation must be reduced by 50%. In the case of a revised certification of precompliance, engineering judgement must be used to ensure that the "conservative" kiln dust metal concentration will not be exceeded. Examples of how this goal might be accomplished include:
    - Changing equipment or operating procedures to reduce the kiln dust metal concentration;
    - Changing equipment or operating procedures, or using more detailed engineering judgement, to decrease the estimated

- SEF and thus increase the "conservative" kiln dust metal concentration limit;
- Increasing the "conservative" kiln dust metal concentration limit by imposing a stricter PM emissions standard; or
- Increasing the "conservative" kiln dust metal concentration limit by performing a more detailed risk assessment to increase the metal emission limits.
- Meanwhile, the facility must continue with daily kiln dust metals monitoring (Step 5).

#### A.1 Determination of Enrichment Factor

After at least 10 initial emissions tests are performed, an enrichment factor for each metal must be determined. At the 95% confidence level, the enrichment factor,  $EF_{952}$ , is based on the test results and is statistically determined so there is only a 5% chance that the enrichment factor at any given time will be larger than  $EF_{952}$ . Similarly, at the 99% confidence level, the enrichment factor,  $EF_{992}$ , is statistically determined so there is only a 1% chance that the enrichment factor at any given time will be larger than  $EF_{992}$ .

For a large number of samples (n > 30),  $EF_{952}$  is based on a normal distribution, and is equal to:

$$EF_{958} = \overline{EF} + z_c \sigma \tag{1}$$

where:

$$\overline{EF} = \frac{\sum_{i=1}^{n} EF_i}{D} \tag{2}$$

$$\sigma = \left[\frac{\sum_{i=1}^{n} (EF_i - \overline{EF})^2}{n}\right]^{\frac{1}{2}} \tag{3}$$

For a 95 % confidence level, z<sub>c</sub> is equal to 1.645.

For a small number of samples (n < 30),  $EF_{952}$  is based on the t-distribution and is equal to:

$$EF_{esk} = \overline{EF} + t_c S \tag{4}$$

where the standard deviation, S, is defined as:

$$S = \left[\frac{\sum_{i=1}^{n} (EF_i - EF)^2}{n-1}\right]^{\frac{1}{2}}$$
 (5)

 $t_c$  is a function of the number of samples and the confidence level that is desired. It increases in value as the sample size decreases and the confidence level increases. The 95% confidence level is used in this method to calculate the "violation" kiln dust metal concentration limit; and the 99% confidence level is sometimes used to calculate the "conservative" kiln dust metal concentration limit. Values of  $t_c$  are shown in Table A-1 for various degrees of freedom (degrees of freedom = sample size - 1) at the 95% and 99% confidence levels. As the sample size approaches infinity, the normal distribution is approached.

# A.2 Comparison of Enrichment Factor Groups

To determine if the enrichment factors measured in the quarterly tests are significantly different from the enrichment factors determined in the initial Step 2 tests, the t-test is used. In this test, the value  $t_{meas}$ :

$$t_{mes} = \frac{\overline{EF_1} - \overline{EF_2}}{\sigma_t \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}}}$$
 (6)

Table A-1 t-Distribution

	<b></b> .	
n-1 or n <sub>1</sub> +n <sub>2</sub> -2	t <sub>.95</sub>	t <sub>.99</sub>
1	6.31	31.82
2	2.92	6.96
3	2.35	4.54
4	2.13	3.75
5	2.02	3.36
6	1.94	3.14
7	1.90	3.00
8	1.86	2.90
9	1.83	2.82
10	1.81	2.76
11	1.80	2.72
12	1.78	2.68
13	1.77	2.65
14	1.76	2.62
15	1.75	2.60
16	1.75	2.58
17	1.74	2.57
18	1.73	2.55
19	1.73	2.54
20	1.72	2.53
25	1.71	2.48
30	1.70	2.46
40	1.68	2.42
60	1.67	2.39
120	1.66	2.36
6	1.645	2.33

$$\sigma_{c} = \left(\frac{(n_{1}-1)S_{1}^{2} + (n_{2}-1)S_{2}^{2}}{n_{1}+n_{2}-2}\right)^{\frac{1}{2}}$$
 (7)

is compared to  $t_{\rm crit}$  at the desired confidence level. The 95% confidence level is used in this method. Values of  $t_{\rm crit}$  are shown in Table A-1 for various degrees of freedom (degrees of freedom =  $n_1$  +  $n_2$  - 2) at the 95% and 99% confidence levels. If  $t_{\rm meas}$  is greater then  $t_{\rm crit}$ , it can be concluded with 95% confidence that the two groups are not from the same population.

#### A.3 Rejection of Data

If the concentration of any hazardous metal in the "required" kiln dust sample exceeds the kiln dust metal concentration limit, the "spare" samples are analyzed. If the average of the combined "required" and "spare" values is still above the limit, a statistical test is used to decide if the upper value can be rejected.

The "Q-test" is used to determine if a data point can be rejected. The difference between the questionable result and its neighbor is divided by the spread of the entire data set. The resulting ratio,  $Q_{meas}$ , is then compared with rejection values that are critical for a particular degree of confidence, where  $Q_{meas}$  is:

$$Q_{\text{meas}} = \frac{DMC_{highest} - DMC_{next \ highest}}{DMC_{highest} - DMC_{lowest}}$$
(8)

The 90% confidence level for data rejection is used in this method. Table A-2 provides the values of  $Q_{\rm crit}$  at the 90% confidence level. If  $Q_{\rm meas}$  is larger than  $Q_{\rm crit}$ , the data point can be discarded. Only one data point from a sample group can be rejected using this method.

Table A-2 Critical Values for Use in the Q-Test

n	Q <sub>crit</sub>
3	0.94
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

#### **ENVIRONMENTAL PROTECTION AGENCY**

40 CFR Parts 260, 261, 264, 265, 266,. 270, and 271

91-012

[EPA/OSW-FR-90=; SWH-FRL-]

Burning of Hazardous Waste in Boilers and Industrial Furnaces

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final Rule.

SUMMARY: Under this final rule, the Environmental Protection Agency (EPA) is expanding controls on hazardous waste combustion to regulate air emissions from the burning of hazardous waste in boilers and industrial furnaces. Currently, such burning is exempt from regulation. EPA is promulgating this final rule after considering public comment on rules proposed on May 6, 1987, plus the comments on EPA's supplemental notices of October 26, 1989 and April 27, 1990.

These rules control emissions of toxic organic compounds, toxic metals, hydrogen chloride, chlorine gas, and particulate matter from boilers and industrial furnaces burning hazardous waste. In addition the rules subject owners and operators of these devices to the general facility standards applicable to hazardous waste treatment, storage, and disposal facilities. Further, today's final rule subjects hazardous waste storage units at regulated burner facilities to Part 264 permit standards. Burner storage operations at existing facilities are generally now subject only to interim status standards under Part 265.

Finally, today's rule takes final action on two pending petitions for rulemaking: (1) based on a petition by Dow Chemical Company, EPA is designating halogen acid furnaces as industrial furnaces under §260.10; and (2) based on a petition by the American Iron and Steel Institute, EPA is classifying coke and coal tar fuels produced by recycling coal tar decanter sludge, EPA Hazardous Waste No. KO87, as products rather than solid waste. The rule also makes several technical corrections to regulations dealing with loss of interim status for facilities that achieved interim status as of November 7, 1984.

EFFECTIVE DATE: This final rule is effective on [date six months from promulgation]. Technical corrections to section 270.73 are effective immediately.

ADDRESSES: The official record for this rulemaking is identified as Docket Numbers F-87-BBFP-FFFFF and F-89-BBSP-FFFFF, and is located in the EPA RCRA Docket, Room 2427, 401 M Street SW., Washington, DC 20460. The docket is available for inspection from 9 a.m. to 4 pm., Monday through Friday, except on Federal holidays. The public must make an appointment to review docket materials by calling (202) 475-9327. The public may copy up to 100 pages from the docket at no charge. Additional copies cost \$.15 per page.

FOR FURTHER INFORMATION CONTACT: For general information contact the RCRA Hotline at: (800) 424-9346 (toll-free) or (202) 382-3000 locally. For information on specific aspects of this final rule, contact Dwight Hlustick, Office of Solid Waste (OS-322W), U.S. Environmental Protection Agency, 401 M Street SW., Washington, DC 20460, (703) 308-8460.

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PART ONE: BACKGROUND

# I. Legal Authority

These regulations are promulgated under authority of sections 1006, 2002, 3001 through 3007, 3010, and 7004 of the Solid Waste Disposal Act of 1970, as amended by the Resource Conservation and Recovery Act of 1976, the Quiet Communities Act of 1978, the Solid Waste Disposal Act Amendments of 1980, and the Hazardous and Solid Waste Amendments of 1984, 42 U.S.C. 6905, 6912, 6921 through 6927, 6930, and 6974.

#### II. Overview of the Final Rule

# A. Controls for Emissions of Organic Compounds

Today's rule requires boilers and industrial furnaces to comply with the same destruction and removal efficiency (DRE) standard currently applicable to hazardous waste incinerators: 99.9999% DRE for dioxin-listed waste, and 99.99% DRE for all other hazardous wastes. In addition, the rule controls emissions of products of incomplete combustion (PICs) by limiting flue gas concentrations of carbon monoxide (CO), and where applicable, hydrocarbons (HC) to ensure that the device is operated under good combustion conditions. Finally, emissions testing and health-risk assessment is required for chlorinated dioxins and furans for facilities meeting specified criteria where the potential for significant concentrations may exist.

#### B. Controls for Emissions of Toxic Metals

The rules establish emission limits for 10 toxic metals listed in Appendix VIII of 40 CFR Part 261 based on projected inhalation health risks to a hypothetical maximum exposed individual (MEI). The standards for the carcinogenic metals (arsenic, beryllium, cadmium, and chromium) limit the increased lifetime cancer risk to the MEI to a maximum of 1 in 100,000. The risk from the four carcinogens must be summed to ensure that the combined risk is no greater than 1 in 100,000. The standards for the noncarcinogenic metals (antimony, barium, lead, mercury, silver, and thallium) are based on Reference Doses (RfDs) below which adverse health effects have not been observed.

The standards are implemented through a three-tiered approach. Compliance with any tier is acceptable. The tiers are structured to allow higher emission rates (and feed rates) as the owner or operator elects to conduct more site-specific testing and analyses (e.g., emissions testing, dispersion modeling). Thus, the feed rate limits under each of the tiers are derived based on different levels of site-specific information related to facility design and surrounding terrain. Under Tier I, the Agency has provided very conservative waste feed rate limits in "reference" tables as a function of effective stack height and terrain and land use in the vicinity of the stack and assumed reasonable, worst-case dispersion. The owner or operator demonstrates compliance by waste analysis, not emissions testing or dispersion modeling. Consequently, the Tier I feed rate limits are based on an assumed reasonable, worst-case dispersion scenario, and an assumption that all metals fed to the device are emitted (i.e., no partitioning to bottom ash or product, and no removal by an air pollution control system (APCS)).

Under Tier II, the owner or operator conducts emissions testing (but not dispersion modeling) to get credit for partitioning to bottom ash or product, and APCS removal efficiency. Thus, the Agency has developed conservative emission rate limits in reference tables, again as a function of effective stack height and terrain and land use in the vicinity of the stack. The Agency also assumed reasonable, worst-case dispersion under Tier II.

Under Tier III, the owner or operator would conduct emissions testing and sitespecific dispersion modeling to demonstrate that the actual (measured) emissions do not exceed acceptable levels considering actual (predicted) dispersion. The standards are implemented through limits on specified operating parameters, including hazardous waste feed rate and metals composition, feed rate of metals from all feed streams, combustion chamber temperature, and APCS-specific parameters.

#### C. Controls for Emissions of Hydrogen Chloride and Chlorine Gas

The rules control emissions of hydrogen chloride (HCl) and free chlorine (Cl<sub>2</sub>) under the same general approach as that used for metals. The owner and operator must comply with and implement the HCl and Cl<sub>2</sub> controls in the same manner as for metals.

## D. Emission Standard for Particulate Matter

The rules limit particulate matter (PM) emissions to 0.08 gr/dscf, corrected to 7 percent oxygen (O<sub>2</sub>). This is the same standard that currently applies to hazardous waste incinerators and is intended to supplement the risk-based metals controls. (Metals emissions are generally controlled by limiting feed rates of metals and controlling PM.) Compliance with the standard is demonstrated by emissions testing, and the standard is implemented by operating limits in the permit on parameters including: ash content of feed streams, feed rate of specific feed streams, and air pollution control system operating parameters. All boilers and industrial furnaces must comply with the standard; however, cement and aggregate kilns need not monitor the ash feed rate of all feed streams to demonstrate compliance with the standard given that particulate matter from these devices is generated primarily from raw materials. Instead, the rule provides that these devices must comply with the operating limits on the particulate matter control system to ensure continued operation at levels achieved during the compliance test (under interim status) or trial burn (under the Part B permit application).

#### E. Permitting Procedures

The final rule requires similar permitting procedures for regulated BIFs that apply to hazardous waste incinerators. For example, owners and operators are required to submit a Part B permit application for evaluation in order to be eligible for an operating permit. Permit applications will be called on a schedule considering the relative hazard to human health and environment the facility poses compared to other storage, treatment, and disposal facilities within the Director's purview.

# F. Controls During Interim Status

Today's final rule requires boilers and industrial furnaces that have interim status to comply with substantive emissions controls for metals, HCl, Cl2, particulates, and CO (and, where applicable, HC and dioxins and furans). Owners and operators must certify compliance with the emissions controls under a prescribed schedule, establish limits on prescribed operating parameters, and operate within those limits throughout interim status.

### G. Units Exempt from Air Emissions Standards

The rule conditionally exempts from regulation the following devices: (1) boilers and industrial furnaces that burn small quantities of hazardous waste fuel (i.e., the small quantity burner exemption) and that operate the device under prescribed conditions; (2) smelting, melting, and refining furnaces that process hazardous waste solely for the purpose of metal reclamation and not partially for destruction or energy recovery; and (3) coke ovens if the only hazardous waste they process is K087.

The small quantity burner exemption -- as provided in section 3004(q)(2)(B) -- is a risk-based exemption specifically alluded to in the statute. The exemption is provided only to hazardous waste fuels generated on-site, and is conditioned on a number of requirements, including a one-time notification and recordkeeping.

The Agency is also providing a temporary exemption for metal reclamation furnaces from today's burner standards until we determine how best to apply rules designed for combustion processes to noncombustion metal reclamation operations. (It should be noted that section 3004(q) requires EPA to issue rules controlling air emissions from devices burning hazardous waste for energy recovery by a specified date. Section 3004(q) does not apply to devices burning hazardous waste for the sole purpose of material recovery. Although EPA has authority to issue such regulations, the section 3004(q) deadline does not apply.) To distinguish between wastes that are processed solely for metal reclamation rather than (partial) destruction, the final rule considers a hazardous waste processed by a smelting, melting, or refining furnace with a total concentration of Appendix VIII, Part 261 toxic organic constituents exceeding 500 ppm to be burned at least partially for treatment or destruction. To distinguish between processing for material recovery and burning for energy recovery, the final rule considers a hazardous waste processed by a metal reclamation furnace with a heating value exceeding 5,000 Btu/lb to be burned at least partially for energy recovery. Metals reclamation furnaces claiming the exemption must

notify the Agency, sample and analyze their hazardous wastes to document compliance with the conditions of the exemption, and keep records of such documentation.

Coke ovens are exempt from today's rule if the only hazardous waste they process is K087 as an ingredient to produce coke. Given that K087 is for practical purposes just like other materials used to produce coke and comes from the same process as these other materials, it would be anomalous to assert RCRA control over the coking process.

#### H. Pollution Prevention Impacts

This rule provides an incentive to reduce the generation of metal and chlorine-bearing hazardous waste at the source given that the metals and HCl emissions controls will be implemented by additional requirements attendant to the disposal of those wastes, i.e., feed rate limits for individual metals and total chlorine. These requirements are, in essence, tied to the economics of disposing of given volumes of waste since feed rates depend, in part, on the volume of waste the facility operator needs to burn. Thus, the metals and HCl controls do not simply require a percent reduction in emissions, irrespective of the volume and rate of incoming waste streams. Rather, the controls are health-based and, thus, provide limits on emissions rates of metals and HCl that would be implemented by feed rate limits.

Waste generators who send their waste to industrial furnaces such as cement kilns and light-weight aggregate kilns that act as commercial waste management facilities will have the incentive to reduce the generation of metal and chlorine-bearing wastes because waste management fees are likely to increase for such waste given that the burner has a fixed metal and chlorine feed rate allotment (due to prescribed feed rates and facility operating conditions). Wastes with extremely high metals content may no longer be acceptable for burning in many cases unless the waste generator reduces the metals content of the waste. Any alternative for the disposal of such wastes may be unavailable or the costs of such treatment may be high enough to create the incentive to reduce waste generation rates at the source. This is a typical scenario for pollution prevention measures to be undertaken by waste generators.

Similarly, generators who burn their wastes on site also have the incentive to reduce the generation of metal and chlorine-bearing wastes given that the rule will provide a fixed feed rate allotment for their boiler or industrial furnace.

### III. Relationship to Other Rules

# A. Regulations to be Promulgated Under the New Clean Air Act

Title III of the recent Clean Air Act Amendments of 1990, amending section 112 of the Act dealing with hazardous air pollutants, potentially addresses many of the same sources that would be regulated under today's rule. That section requires the Agency to develop a list of major and area sources of hazardous air pollutants (a major source is a stationary source that has the potential to emit up to 10 tons per year of a hazardous air pollutant, or 25 tons per year of a combination of such pollutants, and area sources are other stationary sources emitting hazardous air pollutants), and to develop technologybased controls for such sources over specified time periods. See Clean Air Act, amended sections 112(c), and (d). Additional controls shall be imposed within eight years after promulgation of each of these technology-based standards, if such controls are needed to protect public health with an ample margin of safety, or to prevent adverse environmental effect. (Cost, energy, and other relevant factors must be considered in determining whether regulation is appropriate in the case of environmental effects.) In addition, if the technology-based standards for carcinogens do not reduce the lifetime excess cancer risk for the most exposed individual to less than one a million (10-6), then EPA must promulgate health-based standards. See amended section 112(f)(2)(A).

It is premature for the Agency to attempt to provide a definitive opinion on the relationship of these provisions to today's rule. Sources covered by the present rule may not ultimately be required to be further regulated under amended section 112. In this regard, amended section 112(n)(7) provides that if sources' air emissions are regulated under subtitle C, "the Administrator shall take into account any regulations of such emissions ... and shall, to the maximum extent practicable and consistent with the provisions of this section, ensure that the requirements of such subtitle and this section are consistent." Thus, at a minimum, Congress was concerned about the potential for duplicative regulation and urged the Agency to guard against it. Since the Agency regards today's rules as protective (based on present knowledge), it may be possible to avoid further air emissions regulation. (EPA notes, however, that these sources will likely be listed as major sources, and the Agency will study whether further emissions controls are required in the course of implementing amended section 112.)

## B. April 27, 1990 Proposed Incinerator Amendments

On April 27, 1990 (55 FR 17862), EPA proposed amendments to the existing hazardous waste incinerator standards of Subpart O, Part 264 to make the incinerator standards conform to the emissions standards being promulgated today for boilers and industrial furnaces burning hazardous waste. The proposed rule would add emission standards for products of incomplete combustion (i.e., carbon monoxide and hydrocarbon limits), metals, and hydrogen chloride and chlorine gas.

In the proposed rule for incinerators, EPA also proposed to revise or to add definitions for a number of thermal treatment devices: industrial furnace, incinerator, plasma arc and infrared incinerators. Those definitions are being promulgated in today's rule. In addition, EPA proposed in the incinerator rulemaking to clarify the regulatory status of carbon regeneration units and fluidized bed incinerators. Those clarifications are also promulgated in today's final rule.

Finally, EPA proposed to revise the definition of principal organic hazardous constituents (POHCs) used to demonstrate destruction and removal efficiency (DRE). The revised definition would allow the Director on a case-by-case basis to approve as POHCs compounds that are neither constituents in the hazardous waste nor organic. That revised definition of POHC is finalized in today's rule as a part of the DRE standard to control organic emissions from boilers and industrial furnaces.

# C. July 28, 1990 Proposed Amendment to Definition of Wastewater Treatment Unit to Exempt Sludge Dryers

On July 28, 1990 (see 55 FR 29280), EPA proposed to clarify the regulatory status of sludge dryers to make it clear that sludge dryers that meet the definition of a tank and that were a part of a wastewater treatment unit were exempt from RCRA regulation even if they heretofore met the definition of an incinerator. Today's final rule promulgates a definition of sludge dryer and revises the definition of incinerator to explicitly exclude sludge dryers. See Part Four, section II of today's preamble.

#### D. Land Disposal Restriction Standards

In the May 6, 1987 proposal, the Agency indicated that once the present rules became final, the Agency would amend certain of the land disposal restriction standards

that specified incineration as a treatment standard (at that time, the standard for HOCs under the California list rule), to also include burning in boilers and industrial furnaces. See 52 FR at 17021. Since that time, the issue has become more involved. In particular, significant issues regarding the relationship of the Bevill amendment and land disposal restrictions exist (which the Agency in fact referenced in the rulemaking record to the California list rule when considering this issue). The Agency believes it inappropriate to try and resolve these issues in this proceeding, given the time. Onstraints created by the District Court's order and the fact that this rulemaking does not deal principally with issues relating to the land disposal restrictions program. The Agency consequently plans to address these questions in a later proceeding and not to finalize the May 1987 proposal at this time.

# PART TWO: DEVICES SUBJECT TO REGULATION

#### I. Boilers

EPA defines a boiler in §260.10 as an enclosed device using controlled flame combustion and having the following characteristics: (1) the combustion chamber and primary energy recovery section must be of integral design; (2) thermal recovery efficiency must be at least 60 percent; and (3) at least 75 percent of the recovered energy must be "exported" (i.e., not used for internal uses such as preheating of combustion air or fuel, or driving combustion air fans or feed water pumps).

Today's final rule applies to all boilers burning hazardous waste for any purpose -energy recovery or destruction. (We note, however, that an existing boiler may not burn
hazardous waste for destruction (i.e., waste that is not a fuel) before certifying compliance
with the interim status emissions standards.)

Nonindustrial boilers are currently prohibited from burning hazardous waste unless they are operated in conformance with the incinerator standards of Subpart O of Parts 264 or 265. On the effective date of today's rule, however, nonindustrial boilers burning hazardous waste will be subject to these boiler and industrial furnace rules. We note that nonindustrial boilers generally cannot burn hazardous waste until they receive an operating permit under today's rule (unless they are already operating under the incinerator standards). This is because the prohibition is not rescinded until the effective date of the rule, and a facility would have to be "in existence" with respect to hazardous waste burning on that date to be eligible for interim status.

EPA believes that approximately 925 boilers burn hazardous waste fuels. Approximately 600 of these boilers burn very small quantities of hazardous waste and will be conditionally exempt under the small quantity burner provision of today's rule. See \$266.109. (We note that these boilers burn less than one percent of the total hazardous waste currently being burned in boilers and industrial furnaces.) EPA also believes that approximately 200 boilers will stop burning hazardous waste because they burn quantities exceeding the small quantity burner exemption but do not burn enough waste to justify the cost of complying with today's rule. Thus, approximately 125 boilers will continue to burn hazardous waste and will be subject to the interim status and permit standards provided by §§266.102 and 266.103 of today's rule.

#### II. Industrial Furnaces

Under today's revised definition, EPA defines an industrial furnace in §260.10 as those designated devices that are an integral component of a manufacturing process and that use thermal treatment to recover materials or energy. With the addition of halogen acid furnaces by today's rule, the Agency has designated 12 devices as industrial furnaces: cement kilns; lime kilns; aggregate kilns (including light-weight aggregate kilns and aggregate drying kilns used in the asphaltic concrete industry); phosphate kilns; coke ovens; blast furnaces; smelting, melting, and refining furnaces; titanium dioxide chloride process oxidation reactors; methane reforming furnaces; pulping liquor recovery furnaces; and combustion devices used in the recovery of sulfur values from spent sulfuric acid. The definition also includes criteria and procedures for designating additional devices as industrial furnaces.

Any industrial furnace burning or processing any hazardous waste for any purpose -- energy recovery, material recovery, or destruction -- is subject to today's rule, with certain exceptions. Furnaces (like boilers) burning small quantities of hazardous waste fuel are exempt from regulation under §266.108, coke ovens are exempt from regulation if the only hazardous waste they burn is Hazardous Waste No. K087, and regulation of smelters processing hazardous waste solely for material recovery is deferred (see discussion in section II.D).

The Agency believes that approximately 75 industrial furnaces burn over one million tons of hazardous waste annually. The regulated universe appears to comprise

approximately 40 cement kilns, 18 light-weight aggregate kilns, and 15 halogen acid furnaces. Each of these types of furnaces is described below.

#### A. Cement Kilns

Cement kilns are horizontal inclined rotating cylinders, refractory lined and internally fixed, to calcine a blend of 80% limestone and 20% shale to produce Portland cement. There is a wet process and a dry process for producing cement. In the wet process, the limestone and shale are ground wet and fed into the kiln in a slurry. In the dry process, raw materials are ground dry. Wet process kilns are longer than dry process kilns in order to facilitate water evaporation from the wet raw material. Wet kilns can be more than 450 feet in length. Dry kilns are more thermally efficient and frequently use preheaters or precalciners to begin the calcining process before the raw material is fed into the kiln.

Combustion gases and raw materials move counterflow in kilns. The kiln is inclined, and raw materials are fed into the upper end while fuels are normally fed into the lower end. Combustion gases thus move up the kiln counter to the flow of raw materials. The raw materials get progressively hotter as they travel the length of the kiln. The raw materials eventually begin to soften and fuse at temperatures between 2,250 and 2,700°F to form the clinker product. Clinker is then cooled, ground, and mixed with other materials such as gypsum to form Portland cement.

Combustion gases leaving the kiln typically contain from 6 to 30% of the feed solids as dust. Particulate emissions are typically controlled with electrostatic precipitators or fabric filters (baghouses), and are often recycled to the kiln feed system.

Dry kilns with a preheater or precalciner often use a by-pass duct to remove from 5 to 30% of the kiln off-gases from the main duct. The by-pass gas is passed through a separate air pollution control system to remove particulate matter. By-pass dust is not reintroduced into the kiln system to avoid a build-up of metal salts that can affect product quality.

Some cement kilns burn hazardous waste fuels to replace from 25 to 75% of normal fossil fuels. Most kilns burn liquid waste fuels but several burn small (e.g., six gallon) containers of viscous or solid hazardous waste fuels. Containers have been fired into the upper, raw material end of the kiln and at the midpoint of the kiln.

Several cement companies have also expressed an interest in using solid hazardous waste such as contaminated soils as an ingredient to produce cement. Cement kilns that burn hazardous waste as an ingredient are regulated by today's rule. Under today's rule, a facility may burn (or process) hazardous waste solely as a bona fide ingredient during interim status beginning with the effective date of the rule. If a waste is burned partially for destruction or energy recovery, however, it is not burned solely as an ingredient and special restrictions apply during interim status (see discussion below). EPA considers a waste to be burned at least partially for destruction if it contains a total of 500 ppm or more by weight of nonmetal hazardous constituents listed in Appendix VIII, Part 261. Further, EPA considers a waste to be burned at least partially for energy recovery if it has a heating value of 5,000 Btu/lb or more.

Today's rule does not allow burning of a waste for the purpose of destruction during interim status prior to certification of compliance (see §266.103(c)) with all applicable emission standards. Further, the rule applies special requirements during interim status on owners/operators who feed hazardous waste into a kiln system at any location other than the "hot" end where product is discharged. Hazardous waste burned (processed) solely as an ingredient, however, is not subject to the special requirements because emissions from such burning would not pose an adverse effect on human health and the environment.<sup>2</sup>

#### B. Light-Weight Aggregate Kilns

Light-weight aggregate (LWA) describes a special use aggregate with a specific gravity much less than sand and gravel which is used to produce insulation and nonstructural and light-weight concrete. LWA is produced much like cement, but the feedstocks are special clays, pumice, scoria, shale, or slate.

The LWA kiln is configured much like a cement kiln. The raw material is crushed and introduced at the upper end of a rotary kiln. In passing through the kiln, the materials reach temperatures of 1,900 to 2,100°F. Heat is provided by a burner at the lower end of the kiln where clinker is discharged.

<sup>1</sup> See discussion in section VII.H of Part Three of the text.

This is because nonmetal toxic constituents will not be present in the waste at significant levels (i.e., less than 500 ppm) and metal emissions will be adequately controlled under today's rule by the air pollution control system irrespective of where the waste is fed into the kiln system.

LWA kilns are also major sources of particulate emissions and are equipped with wet scrubbers, fabric filters, or electrostatic precipitators. Wet scrubbers dominated the industry until recently. Many facilities are now converting to dry systems to reduce the cost of residue management by recycling the collected dust into the kiln.

LWA kilns that burn hazardous waste fuel typically burn 100% liquid hazardous waste fuels.

#### C. Halogen Acid Furnaces

The Dow Chemical Company (DOW) filed a rulemaking petition with EPA on March 31, 1986, in accordance with the provisions of 40 CFR 260.20, requesting that EPA designate their halogen acid furnaces (HAFs) as industrial furnaces. HAFs are typically modified firetube boilers that process secondary waste streams containing 20 to 70 percent chlorine or bromine to produce a halogen acid product by scrubbing acid from the combustion gases. Currently HAFs that produce steam meet the definition of a boiler while HAFs that do not generate steam meet the definition of an incinerator even though they use hazardous waste as a fuel and as an ingredient to produce halogen acid product. Today's rule designates HAFs that do not generate steam as an industrial furnace for the reasons given below.

DOW petitioned the Agency to designate their HAFs as industrial furnaces after the Agency changed the definition of incinerator in 1985 from a "purpose of burning test" to a "design test" and developed new classifications for boilers and industrial furnaces. The Agency inadvertently did not designate HAFs as industrial furnaces at that time which potentially left certain HAFs operating not in compliance with the incinerator standards promulgated in 1981. Although HAFs (prior to today's rule) technically meet the definition of incinerator, the Agency has indicated its intention since receiving the DOW petition to correct the problem and to properly designate HAFs as industrial furnaces.

On May 6, 1987 (52 FR 17033), EPA proposed to grant this petition and to add halogen acid furnaces (HAFs) to the list of devices that are designated as industrial furnaces under 40 CFR 260.10. On April 27, 1990 (55 FR 17917), the Agency proposed changes to the proposed designation of HAFs as industrial furnaces. With modifications based on additional information and comments, today's rule adds HAFs to the list of devices that are included in the definition of an industrial furnace under 260.10.

In today's rule, EPA is defining an "industrial furnace" in 260.10 as an enclosed device that uses thermal treatment to recover (or produce) materials or energy as an integral component of a manufacturing process.<sup>3</sup> EPA has previously designated 11 devices as industrial furnaces: (1) cement kilns; (2) lime kilns; (3) aggregate kilns (including lightweight aggregate kilns and aggregate drying kilns used in the asphaltic concrete industry); (4) phosphate kilns; (5) coke ovens; (6) blast furnaces; (7) smelting, melting, and refining furnaces; (8) titanium dioxide chloride process oxidation reactors; (9) methane reforming furnaces; (10) pulping liquor recovery furnaces; and (11) combustion devices used to recover sulfur values from spent sulfuric acid.

The industrial furnace definition in 260.10 also provides criteria and procedures for adding devices to the list. A device may be defined as an industrial furnace if it meets one or more of the following criteria: (1) the device is designed and used primarily to recover material products; (2) the device is used to burn or reduce raw materials to make material products; (3) the device is used to burn or reduce secondary materials as effective substitutes for raw materials in processes that use raw materials as principal feedstocks; or (4) the device is used to burn or reduce secondary materials as ingredients in industrial processes to manufacture material products.

As explained below, the basis for designating HAFs as industrial furnaces under 260.10 is that HAFs are integral components of a manufacturing process, they recover materials and energy, and they meet two of the criteria (1 and 4) described above for classifying a device as an industrial furnace.

1. Current Practices. Information available to EPA indicates that at least 3 companies in the United States operate at least 30 devices that may be halogen acid furnaces. These devices typically process chlorinated or brominated secondary materials with 20 to 70 percent halogen content (by weight) to produce an acid product, either hydrogen chloride (HCl) or hydrogen bromide (HBr), both of which have a halogen content that ranges from 3 to greater than 25 percent (by weight). These secondary

This definition of industrial furnace is the revised definition as noticed on April 27, 1990 (55 FR 17869). The previous definition read "an enclosed device using controlled flame combustion to recover materials or energy as an integral component of a manufacturing process." Public comments on the proposal are discussed in the Comment Response Document for the BIF Regulations. EPA revised the definition to include nonflame devices (i.e., by referring to thermal treatment) because controlled-flame devices and nonflame devices can have the same emissions and pose the same hazard to human health and the environment.

materials typically have as-fired heating values of approximately 9,000 Btu/lb and are typically produced on site.

Some of the HAFs currently in use are modified firetube boilers that generate and export steam. These HAFs meet the definition of a boiler under §260.10, and, thus, will be regulated as boilers. The remaining HAFs, although modified firetube boilers, do not generate steam and thus do not meet EPA's definition of a boiler. Today's rule classifies these nonboiler HAFs as industrial furnaces. For the remainder of this discussion, the term "HAF" refers to these nonboiler HAFs.

#### 2. Designation of HAFs as Industrial Furnaces.

- a. Dow's Petition. On March 31, 1986, the Dow Chemical Company (DOW) filed a rulemaking petition with EPA in accordance with the provisions of 40 CFR 260.20, requesting that HAFs at Dow Chemical be designated as industrial furnaces. EPA proposed to grant this petition in the May 6, 1987 proposal. Today's rule includes HAFs in the definition of an industrial furnace under §260.10. Further background discussion on DOW's petition is contained in the May 6, 1987 proposed rule.
- b. May 1987 and April 1990 Proposed Rules. EPA proposed to designate HAFs as industrial furnaces for the reasons discussed in the May 6, 1987 proposed rule. To ensure that a particular device was an industrial furnace involved in bona fide production of acid<sup>4</sup> as an integral component of a manufacturing process, and was not an incinerator equipped with halogen emissions removal devices, the 1987 proposed HAF definition required that: (1) the furnace be located on site at a chemical production facility; (2) the waste fed to the device be halogenated; and (3) the acid product from the device contain at least 6 percent halogen acid.

Based on comments received on the 1987 proposal and on further consideration by the Agency, EPA proposed revisions to the HAF definition in the April 1990 notice. These revisions were proposed for two reasons: (1) to better clarify the differences between

The Agency's concern is that devices capturing some HCl in scrubber effluent not automatically be classified as HAFs if they find a way to utilize the scrubber effluent. The HCl content of the effluent from wet scrubbers used to control HCl emissions from the incineration of chlorine-bearing waste is normally on the order of 1 percent or less. EPA does not consider such low HCl content scrubber water a bona fide product for purposes of designation as an industrial furnace even if the scrubber water is beneficially used in a manner that specifically relates to its HCl content.

HAFs and incinerators equipped with wet scrubbers to control halogen acid emissions, and (2) to bener reflect industry practice.

To ensure that a particular device is an integral component of a chemical manufacturing process, the April 1990 proposal included requirements that at least 50 percent of the acid product be used on site and that any off-site waste fed to the HAF be generated by a SIC 281 (inorganic chemicals) or SIC 286 (organic chemicals) process. To ensure that the waste is burned as a bona fide ingredient to produce the halogen acid product, the April 1990 proposal also required that each waste fed to the HAF have an "asgenerated" halogen content of at least 20 percent. In addition, to better reflect industry practice, the 1990 proposal required that the acid product have a halogen acid content of 3 percent rather than 6 percent, an amount that still clearly distinguished the HAF acid product from incinerator scrubber water, which has an acid content of well below 1 percent. Finally, EPA proposed in April 1990 to list hazardous waste fed to a HAF as inherently waste-like to ensure that halogenated waste fed to a HAF (and the HAF itself) would be subject to regulation. This would preclude a claim that the secondary materials were used as ingredients to make a product, and, thus, not a solid waste under \$261.2(e)(1)(i).

c. Summary of Public Comments. Commenters on the 1987 and 1990 proposed rules objected to the requirements that 50 percent of the acid product be used on site and that any off-site waste feed be limited to SIC 281 or 286 processes. The commenters argued that minimum specifications on the halogen content of the feed and/or the acid content of the HAF product are sufficient to distinguish bona fide HAF operations from incinerator operations, and that the requirement that a substantial portion of the product be used on site serves only to limit the legitimate treatment of halogenated wastes and the sale of bona fide HAF products without being necessary to protect human health and the environment.

After consideration of these commenters' concerns, the Agency believes that both the proposed off-site restriction for waste fed to HAFs and the proposed on-site acid product use restriction are indeed unnecessary to ensure that HAFs are integral components of manufacturing processes. The Agency agrees with the commenters that the requirements specifying the minimum halogen content of the waste feed and the minimum halogen acid concentration of the HAF product are sufficient to ensure that HAFs are integral components of a manufacturing process (i.e., the process of halogen acid production). EPA is not adopting these proposed conditions given that air emissions from HAFs will be

regulated under today's rule, that these proposed conditions were directed at how to classify these devices rather than how to ensure their safe operation, and that HAF operations (as properly controlled) are environmentally advantageous in that they utilize acid values rather than dispose them and therefore should not needlessly be discouraged. Today's rule, therefore, does not restrict the use of HAF waste feeds generated off site or require that any percentage of the acid product be used on site.

In today's rule, the Agency considers a bora fide HAF operation as one in which a secondary material with a minimum as-generated halogen content of 20 percent by weight is processed into an acid product with a minimum halogen content of 3 percent by weight. The acid product must be used in a manufacturing process either on site or off site. The Agency maintains that this approach will allow the legitimate processing of highly halogenated secondary materials into usable products but will still clearly distinguish HAF product acid from incinerator halogen acid scrubber water.

Upon review of other comments submitted on the 1987 and 1990 proposed rules, the Agency has identified several issues pertaining to HAFs that require clarification in the regulations. Specifically, these issues concern: (1) the regulation of chlorine emissions from HAFs, (2) the operation of HAFs under the special operating requirements (SOR) exemption for boilers, and (3) the designation of hazardous waste fed to HAFs as inherently waste-like material.

One commenter to the 1987 proposed rule requested that the Agency clarify its position on limiting inorganic halide salts in feedstocks to boilers and industrial furnaces. The Agency has established limits on emissions of HCl and Cl<sub>2</sub> from industrial furnaces, and a HAF operator, like any other industrial furnace operator, must comply with these HCl and Cl<sub>2</sub> emission standards. To demonstrate compliance under the Tier I feed rate screening limits, a HAF operator must include inorganic chlorine as part of the total chlorine fed to the device. The Agency believes that this requirement is justified because recent testing indicates that even thermally stable compounds such as NaCl are converted with high efficiency to HCl under laboratory conditions that simulate incineration.<sup>5</sup>

Another commenter to the 1987 proposal stated that HAFs are unjustly excluded from the automatic waiver of a trial burn to demonstrate 99.99% destruction and removal efficiency (DRE) when operated under the special operating requirements (SORs). The

U.S. EPA, <u>Laboratory Method to Estimate Hydrogen Chloride Emission Potential</u>
Before Incineration of a Waste, February 1990.

Agency acknowledges the commenter's concern, but notes that all industrial furnaces, including HAFs, are ineligible for the automatic DRE trial burn waiver. The Agency stated in the preamble to the 1987 proposal that modified boilers that produce and export steam (and thus meet EPA's definition of boiler in 260.10) would be regulated as boilers. In such a case, the unit may be eligible for the automatic waiver of the DRE trial burn, which applies only to boilers. Any halogen acid furnace that is a modified fire-tube boiler not meeting the definition of a boiler in 260.10, however, would not be eligible for the automatic waiver. The Agency's reasons for applying the automatic DRE trial burn waiver only to boilers are discussed further in Section II.C.2.d of this preamble.

Several commenters expressed concern that the April 27, 1990 proposal required a minimum heating value of 5,000 Btu/lb for secondary materials fed to HAFs. Today's final rule does not require a minimum heating value on secondary materials fed to HAFs. Although the Agency understands that most wastes burned in HAFs have a heating value greater than 5,000 Btu/lb and, so, the HAFs are engaged in energy recovery as well as materials recovery, not all wastes meeting the minimum halogen limit also have a heating value normally associated with energy recovery. The Agency believes that HAFs need not be required to recover both material and energy values from every hazardous waste fed to the device to meet the definition of an industrial furnace, and that the regulations adopted today for HAFs ensure that they will be operated in a protective manner even if energy values are not recovered.

Commenters' misconceptions regarding a minimum heating value for secondary materials may have arisen from the Agency's proposal pursuant to §261.2(d)(2) to list hazardous waste fed to HAFs as inherently waste-like material. In today's rule, the Agency is listing as inherently waste-like any secondary material fed to HAFs that is identified or listed as a hazardous waste under 40 CFR Part 261, Subparts C and D. Without such materials being designated as inherently waste-like, HAFs burning hazardous wastes solely as ingredients (i.e., wastes that have low heating value and therefore, are not burned partially for energy recovery) to produce an acid product might not be regulated because the material they are burning might not be a solid waste pursuant to §261.2(e)(1)(i). However, HAFs that burn hazardous wastes with high heating values (i.e., greater than 5,000 Btu/lb), would be subject to today's rule even without listing them as inherently waste-like because these wastes are considered under §261.2(e)(2)(ii) to be burned at least partially for energy recovery. For reasons discussed in the April 27, 1990 proposed rule (55 FR 17892), the Agency believes that such an inconsistent result would

not provide adequate protection of human health and the environment (the wastes burned by HAFs are some of the most toxic generated and regulation of emissions from burning these wastes certainly is needed to protect human health and the environment). Moreover, there are significant elements of treatment associated with burning in HAFs: toxic organic compounds are destroyed rather than recovered, and the burning if conducted improperly could become part of the waste disposal problem. Because the materials burned in HAFs meet the criteria of §261.2(d) for inherently waste-like materials, EPA today is adding to the list of inherently waste-like materials under §261.2(d)(2) secondary materials fed to HAFs that are listed or identified as hazardous waste under Subparts C or D of Part 261. While HAFs will not be precluded from burning secondary materials with low heating values, today's listing will prevent the HAFs that burn this material and the material itself from being unregulated. As a result, in all cases, hazardous waste fed to HAFs, and the HAFs themselves, will be subject to hazardous waste regulations under today's final rule.

d. Basis for Designating HAFs as Industrial Furnaces. EPA has defined an industrial furnace in §260.10 as any of the specifically-designated enclosed devices that are integral components of a manufacturing process and that use thermal treatment to accomplish recovery of materials or energy. To date, 11 types of devices have been designated as industrial furnaces. The industrial furnace definition also provides criteria for adding devices to the list. As discussed above, these criteria include: (1) the design and use of the device primarily to accomplish recovery of material products; (2) the use of the device to burn or reduce raw materials to make a material product; (3) the use of the device to burn or reduce secondary materials as effective substitutes for raw materials in processes using raw materials as principal feedstocks; and (4) the use of the device to burn or reduce secondary materials as ingredients in an industrial process to make a material product. As explained below, HAFs meet the definition of an industrial furnace as well as two of the above criteria, (1) and (4), for designating additional devices as industrial furnaces.

HAFs are Integral Components of a Manufacturing Process. HAFs are commonly located on-site at large scale chemical manufacturing processes that reclaim primarily secondary materials generated on-site and that typically use the halogen acid product on-site. In these cases, the Agency believes the device should clearly be considered an integral component of the manufacturing process and, thus, eligible for designation as an industrial furnace. The situation is less clear when the device receives halogen-bearing secondary materials from off-site or if the halogen acid product is sent off-site. In these situations, the Agency believes, nonetheless, that the device should be considered an integral component

of a manufacturing process and, thus, eligible for consideration as an industrial furnace provided that the device is located on the site of a manufacturing process and that the halogen acid product is used by a manufacturing process.

HAFs Recover Materials and Energy. EPA believes that HAFs recover materials and energy to produce a bona fide product. Production of halogen acid (a 3 to 20 percent halogen acid solution) from the combustion of chlorine-bearing secondary materials constitutes materials recovery in the context of the designation of HAFs as industrial furnaces. HAFs can also be considered to burn secondary materials as ingredients in an industrial process to make a material product (i.e., the product halogen acid). As discussed above, chlorine-bearing secondary materials are burned to produce the halogen acid product for use in a manufacturing operation.

HAFs also recover energy. Most halogen-bearing secondary materials reclaimed in HAFs are burned partially for energy recovery because substantial, usable heat energy is released by the materials during combustion. The materials typically have an as-fired heating value of approximately 9,000 Btu/lb, and the heat released results in the thermal degradation of chlorinated organic compounds to form HCl. Although under definitions in 260.10, energy recovery in a boiler is characterized by the recovery and export of energy, energy recovery in an industrial furnace need not involve any export of energy. Rather, energy recovery in an industrial furnace is based on the burning of materials with substantial heating values (greater than 5,000 Btu/lb) in a manner that results in the release of substantial usable heat energy. See 50 FR 49171-49174 (November 29, 1985).6

HAFs Meet Industrial Furnace Criteria. The Agency believes that HAFs meet two of the above criteria (i.e., criteria (1) and (4)) for designating devices as industrial furnaces. EPA believes that restrictions on the halogen content of waste streams fed to HAFs and on the halogen content of the acid product ensure that the HAF is: (a) designed primarily to recover halogen acid (and so is not engaged in incineration); and (b) used to burn secondary materials as ingredients in the process of halogen acid production to produce a material product (i.e., the product halogen acid).

Addition of HAFs to List of Industrial Furnaces. EPA believes that HAFs are integral components of a manufacturing process and that they are designed and operated to

We note as discussed previously in the text that, although all hazardous wastes fed to a HAF must have an as-generated halogen content of at least 20%, all such wastes need not have a heating value of 5,000 Btu/lb.

recover materials and energy. For these reasons EPA is today adding to the list of devices designated as industrial furnaces under §260.10 HAFs defined as furnaces that: (1) are located at the site of a manufacturing process; and (2) process hazardous wastes with a minimum as-generated halogen content of 20 percent by weight to produce an acid product with a minimum halogen content of 3 percent by weight and where the acid product is used in a manufacturing process.

e. Interim Status for HAFs. HAFs that are in existence on the effective date of today's rule are eligible for interim status like other boilers and industrial furnaces burning for energy or material recovery. Although certain HAFs may technically have met the amended definition of incinerator, EPA believes that there was legitimate confusion as to such units' operating status. These devices would not have been incinerators under the original 1980 definition of incinerator because their primary purpose was not destruction of waste. When EPA amended that definition in 1985 to adopt a definition based on the unit's design rather than its operating purpose, the Agency did not intend to regulate HAFs as incinerators and noted that the regulatory change was not intended to (or expected to) affect the number and identity of regulated incinerator units. See 50 FR 625 (Jan. 4, 1985). Moreover, given that many HAFs met the definition of boiler, it would have been anomalous and unintended for some HAFs to be subject to full regulation and others to be unregulated (until the present rules were adopted). Given these circumstances, the Agency is finding pursuant to §270.10(e)(2) that there was substantial confusion as to which HAF owners and operators were required to submit a Part A application and that this confusion is attributable to ambiguities in the subtitle C rules. Accordingly, such owners and operators may submit Part A applications by the effective date of today's regulation.

We note that this policy on interim status eligibility date does not apply to other devices that are currently subject to regulation as an incinerator but claim to be an industrial furnace subject to the BIF rule and its interim status eligibility date. An example is an aggregate kiln that currently burns hazardous waste for the purpose of treatment (destruction) and, so, is subject to the incinerator standards of Subpart O, Parts 264 and 265. There is no ambiguity about the regulatory status of such a device given that the Agency clearly intended for such burning to be subject to the incinerator standards, and the Agency's rules have always so stated. Thus, the date for interim status eligibility for such facilities is the 1981 date for incinerator interim status.

# D. Smelting, Melting, and Refining Furnaces Burning Hazardous Waste to Recover Metals

In the October 1989 supplement to the proposed rule, EPA solicited further comment on an appropriate regulatory regime for smelting furnaces burning hazardous waste for the exclusive purpose of material recovery. See 54 FR 43733. This issue was closely connected with the question of jurisdictional limitations on the Agency's authority to regulate industrial furnaces burning secondary materials for material recovery, discussed under the rubric of indigenous wastes. Id. at 43731-32. The Agency noted generally that where it did not perceive jurisdictional limitations on its authority, it regarded regulation of organic emissions from smelting furnaces as unnecessary given the normal absence of organics in the material feed to the unit. We also indicated concern at the prospect of regulating emissions of metals that were not attributable to the processing of hazardous waste, and accordingly solicited comment as to a means of determining when burning of hazardous waste resulted in emissions in excess of those from processing other materials in the device. Id. at 43733. With respect to a test for determining when wastes are indigenous, the Agency reproposed a fairly broad test that would have had the effect of excluding many wastes and devices from the Agency's jurisdiction, but would have distinguished between wastes being burned for the purpose of conventional treatment, and for the purpose of material recovery treatment.

These proposals proved extremely controversial. Perhaps more importantly, after the proposal was issued, the question of indigenous waste was the partial subject of the District of Columbia Circuit Court of Appeals' decision API v. EPA, 906 F. 2d 726 (D.C. Cir. 1990). In that decision, the court stated that the Agency had been overly restrictive in interpreting the jurisdictional limitations imposed by the statutory definition of solid waste based upon the court's earlier opinion in American Mining Congress v. EPA, 824 F. 2d 1177 (D.C. Cir. 1987). That earlier opinion, the court held, is limited to situations involving continuous recycling processes that are not part of the waste disposal problem, and certainly does not mandate the type of indigenous principle that the Agency discussed in the 1989 notice. 906 F. 2d at 740-41. The court accordingly remanded and directed the Agency to rethink whether any type of indigenous principle is warranted given the court's clarification of its earlier opinion.<sup>7</sup> Id. at 741.

Technically, the court remanded the Agency's decision not to formally adopt a treatment standard under the land disposal restrictions program for the residue from processing a waste the Agency had indicated would be indigenous to a particular type of

The court's opinion, as well as the many comments on this lisue, raise complex issues that EPA has not yet resolved. (In this regard, the Agency notes that the mandate in section 3004(q) to regulate facilities burning hazardous waste for energy recovery as may be necessary to protect human health and the environment does not apply to devices burning for the purpose of material recovery, H. Rep. No. 198, 98th cong. 1st Sess. 40, and so the court-ordered December 31, 1990 issuance date does not apply.) In particular, the Agency is presently studying the question of jurisdiction as part of a comprehensive effort to determine if the Agency's rules on recycling should be amended (either as a regulatory matter or as part of RCRA reauthorization). In the interim, however, the Agency does not believe it prudent to apply regulations to a whole potential class of devices and wastes that the Agency has not fully evaluated (since these situations would have been excluded from regulation under the proposal). See provision for conditional deferral of smelting, melting, and refining furnaces under §266.100(c). In addition, because EPA has placed most of its efforts into issuing the mandated portion of these regulations as soon as possible, the Agency has not resolved the questions of how to regulate raised in the 1989 notice even for the class of smelting furnaces where authority would have existed under the proposed view of indigenous waste. The issue of whether material recovery is a form of "treatment" is also presently submitted for decision to a panel of the D.C. Circuit in Shell Oil v. EPA (No. 80-1532), and the Agency believes it prudent to await the Court's ruling.

Another reason for deferring regulation of these devices is that the Agency wishes to study further whether regulation under the Clean Air Act may be more appropriate than RCRA regulation. Smelting, melting, and refining furnaces have been traditional subjects of Clean Air Act regulation, and with the advent of amended section 112 of the Clean Air Act amendments of 1990, technology-based controls on toxic air emissions are likely to apply to these devices. Given that in many instances the principal risks potentially posed by air emissions from these devices would come from the nonhazardous waste portion of feed (see 54 FR at 43733), and that Clean Air Act regulation may result in control of individual toxics, the Agency believes that further study of the most appropriate means of regulation is warranted. (The Agency specifically requests information on other devices that may burn hazardous waste solely for metal recovery. EPA will use such information

metal recovery furnace. <u>Id.</u> at 740. EPA has since indicated, in motions filed with the Court, that it views the interim treatment standard based on stabilization as applying in all cases where the residue remains a hazardous waste.

to consider whether the deferral for smelting, melting, and refining furnaces should be broadened provided that the principles stated here apply to the other devices as well.)

At the same time, EPA is concerned that this deferral not become a license for sham recycling activities, or for operations motivated by conventional treatment objectives rather than recovery purposes. Accordingly, the Agency has crafted this deferral narrowly. First, only smelting, melting, and refining furnaces (as used in the §260.10 definition of "industrial furnace"; burning hazardous waste solely to recover metals would be eligible for this deferral. In the unlikely event that one of these devices would be used to recover organics or nonmetal inorganics, EPA believes that substantial amounts of organics would be destroyed showing that the purpose of the activity was either conventional treatment or energy recovery. (The Agency notes specifically that it intends to include as a smelting, melting, or recovery furnace the types of high temperature metal recovery devices used as the basis for the land disposal prohibition treatment standard for waste KO61, and other similar devices.)

Second, sham recovery operations would be viewed as conventional treatment operations and would require a permit to control emissions. Although it is difficult to quantify when operations are sham, two fundamental notions are that any waste involved must contain economically viable amounts of metals to recover (the best objective measure would be the same or greater levels of metal as in normal nonhazardous feed stocks), and that the person recovering the metal be in the business of producing metals for public sale (whether to an ultimate user or for further processing or manufacture). See also 53 FR at 522 (Jan. 8, 1988). The limitations on Btu level and levels on toxic organics discussed below are further efforts to ensure that only bona fide metal recovery activities be deferred from emissions regulation at this time.

Third, today's regulations are deferred only when these devices burn (process) hazardous waste exclusively for metal recovery and not partially for destruction or energy recovery as well. To implement this policy, today's rule provides that a waste with a heating value of 5,000 Btu/lb or more (either as-generated or as-fired) is burned (at least partially) as a fuel. The heating value limit is based on the Agency's long standing sham recycling policy (48 FR 11157 (March 16, 1983)) that wastes with a heating value of 5,000 Btu/lb or more are considered to be fuels. See also 50 FR at 49171-173 (Nov. 29, 1985) (partial burning for energy recovery is covered by section 3004(q) and Btu-rich wastes are burned at least partially for that purpose).

Finally, only wastes that contain less than 500 ppm to: toxic organic constituents listed in Appendix VIII, Part 261, will be considered to recover metals. EPA believes that it is important to have an objective measure to determine when burning is for metal recovery, and that a 500 ppm level is within the zone of reasonable values that the Agency could select for this purpose. As noted in the supplemental proposal in a closely related context, a 500 ppm level for total toxic organic constituents reasonably distinguishes wastes destined for material recovery from wastes burned for nonrecovery purposes because: (1) it represents a concentration of material far exceeding trace levels (generally measured in single digit parts per million (ppm) or tens of ppm); (2) this level of hazardous constituents could create an incremental health risk if burned inefficiently, or with inadequate emission controls; and (3) this level is high enough to indicate that an objective of burning is waste treatment -- destroying nontrace level organics -- as opposed to material recovery. (The Agency's earlier proposal dealt with the question of when a waste might be considered to be indigenous to an industrial furnace burning for material recovery, and considered the issue of whether these devices were burning for a material recovery purpose, and proposed the 500 ppm level adopted in this rule as a means of objectively ascertaining that purpose. 54 FR 43731.)

In order to be informed of persons claiming this deferral, and in order to decrease potential abuse of the deferral, the Agency is requiring that all persons notify the Agency if they assert that their smelting, melting, or refining furnaces are deferred from regulation when burning hazardous wastes because the purpose of the activity is metal recovery. In addition, all such persons have to keep records documenting the basis for the claim (i.e., that the wastes meet the Btu and total toxic organic constituent thresholds, the wastes contain recoverable levels of metals, and the device is indeed engaged in producing a metal product for public use). Sampling and analysis procedures specified in SW-846 must be used to make these determinations. These conditions are consistent with existing §261.2(f) which requires that all persons claiming to be exempt or excluded from regulation because of a recycling activity to have the burden of proof demonstrating that they are entitled to the exemption or exclusion. In addition, the Agency notes that a consistent recommendation of state and regional officials at the Agency's recent public meetings on the regulatory definition of solid waste was to provide notification and recordkeeping so that regulatory officials know that a person is operating in an exempt status in order to verify their claim. The Agency is acting on these recommendations in this rule.

The Agency also notes that the derived from rule could apply to the residues from metal recovery if metals are being recovered from listed hazardous wastes. EPA believes this to be explicit from the remand in API v. EPA discussed earlier. The Court indicated that the Agency's explanation for not establishing a treatment standard for the slag residue from processing waste K061 was erroneous, and remanded the case to the Agency to reconsider its explanation. 906 F. 2d at 740-42. Implicit (or perhaps explicit) in this holding is the fact that the Court viewed the residue as a hazardous waste still coming under the terms of the K061 land disposal prohibition (the Court referred repeatedly to "k061 slag" and mentioned the derived from rule as the basis for the slag being a hazardous waste, id. at 742), at least until the Agency provides a different explanation as to why the slag might not be a hazardous waste. Thus, because EPA has not yet provided a new explanation regarding the indigenous principle (as explained above), at the present time, EPA views residues from metal recovery of listed hazardous wastes are considered to be derived from treatment of hazardous waste and thus hazardous themselves unless some other principle (such as the Bevill amendment, or in some cases, status under an authorized state program) operates to achieve a different result.

Finally, the Agency notes that the deferral applies only to the furnace itself. The hazardous waste is subject to transportation and storage controls prior to introduction into the furnace. See §266.100(c).

The deferral of regulation of emission standards does not apply to cement kilns, aggregate kilns, and HAFs that burn hazardous waste for purposes other than energy recovery. The Agency has studied these devices carefully and determined that the regulatory standards in today's rule are appropriate for these devices when they burn hazardous wastes for a purpose other than energy recovery. Consequently, the Agency sees no reason to defer emission standards for these types of units.

# PART THREE: STANDARDS FOR BOILERS AND INDUSTRIAL FURNACES BURNING HAZARDOUS WASTE

Today's rule establishes controls for emissions of particulate matter, toxic organic compounds, toxic metals, and hydrogen chloride and free chlorine. Those controls are discussed below.

EPA notes that in some cases, today's rule potentially requires limitations on the content of nonwaste input to a boiler or industrial furnace that is burning hazardous waste.

For example, compliance with the limits for metals, PM, and HCl/Cl2 requires controls not only on the hazardous waste input but also potentially controls on other fuels and industrial furnace feedstocks. EPA has adopted this approach not to regulate the nonwaste input to these devices, but rather to ensure that burning hazardous waste in the device does not pose unacceptable risks to human health and the environment. These limitations function as operating conditions on the unit to ensure compliance with the hazardous waste emission standards. For example, unless limitations are established on nonwaste parameters, owners and operators could initially demonstrate compliance by burning clean raw materials along with hazardous waste, and then change their raw material input in a manner that causes emissions to increase significantly. In addition, the approach adopted today allows owners and operators maximum flexibility in demonstrating compliance with the emission standards by allowing adjustments to nonwaste input as a means of achieving compliance. The alternative of demonstrating compliance only through alteration of hazardous waste feed is not only less flexible, but would create enormous administrative difficulties (and add significant expense) for both regulated entities and Agency permit writers. (For example, stack monitoring might no longer be a feasible means of demonstrating compliance because one could not ascertain what portions of the emissions are attributable to burning hazardous waste.) For these reasons, we think the approach adopted today is the most sensible means of demonstrating compliance.

#### I. Emission Standard for Particulate Matter

Boilers and industrial furnaces that burn hazardous waste may emit substantial quantities of particulate matter (PM). (Emissions of particulate matter can have adverse effects on human health and the environment even if toxics are not adsorbed on the particulate matter. However, the Agency's chief concern in this rule is control of adsorbed toxics.) Because toxic metals and organic compounds may adsorb onto smaller size PM that can be entrained in the lungs, unregulated particulate emissions could pose a significant threat to human health. Although there may be limitations to the health-based standards, the metals and organic emissions standards promulgated in today's rule provide protection of public health based on current knowledge about toxic pollutants and available risk assessment methodologies. The PM control standard promulgated today will provide additional protection by ensuring that adsorbed metal and organics are removed from stack gas with the PM.

In today's rule, EPA is establishing a standard for boilers and industrial furnaces which limits particulate emissions to 0.08 gr/dscf (grains/dry standard cubic foot) corrected

to 7% exygen. This limit was chosen because it provides a common measure of protection from particulate emissions from boilers, industrial furnaces, and incinerators burning hazardous waste. This standard may be redundant for: (1) a new, large capacity facility assigned to a specific source category which is governed by a New Source Performance Standard (NSPS); (2) a waste burning facility located in a non-attainment area subject to State Implementation Plan (SIP) standards; (3) a facility with standards for metals and HCl emissions that result in particulate emissions below 0.08 gr/dscf; and (4) a facility subject to a stricter standard based on Best Available Control Technology (BACT) imposed pursuant to the Clean Air Act's Prevention of Significant Deterioration (PSD) program. In such cases, the device would be subject to the more stringent particulate matter standard, not the RCRA 0.08 gr/dscf standard, and the additional burden of demonstrating compliance with the applicable particulate matter standard concurrently with the applicable emissions standards in today's rule for organic compounds, metals, and acid gases will not be substantial. We believe, however, that there are many situations where a BIF is either not currently subject to a particulate matter standard, or the standard is higher than the RCRA 0.08 gr/dscf standard.

The Agency has considered lowering the particulate standard to take advantage of technology advances made in air pollution control and to be consistent with the proposed standard of 0.015 gr/dscf for municipal waste incinerators. (We note that the proposed standard for MWIs also served as a surrogate to control emissions of toxic metals. 54 FR 52219. In contrast, today's rule has separate emission standards for each toxic metal.) We are not prepared to do that at this time, however, because we have not conducted the studies to establish an appropriate PM standard that represents best demonstrated technology (BDT). Although many boilers and industrial furnaces may be able to achieve a PM standard lower than 0.08 gr/dscf (in fact, the PM NSPS for specific types of BIFs is lower than 0.08 gr/dscf), we are not certain that all BIFs can meet a standard of 0.015 gr/dscf. This is because some industrial furnaces have a very high (uncontrolled) particulate loading due to entrained particles of raw materials. Examples are cement kilns and light-weight aggregate kilns. Hence, a single PM standard of 0.015 gr/dscf cannot now be promulgated.

The Agency firmly believes that the 0.08 gr/dscf PM standard, when used as a supplement to the risk-based metal controls provided by today's rule, provides protection of human health and the environment. Given that hazardous waste burned in BIFs could contain virtually unlimited concentrations of toxic metals, the Agency believes that risk-

based standards are needed to supplement the PM standard for hazardous waste burning irrespective of whether the PM standard represents best-demonstrated technology. Even under a PM standard as low as 0.015 gr/dscf, a large fraction of the PM emitted from a hazardous waste combustion device could be comprised of toxic metals that could result in substantial health risk.

Nonetheless, the Agency will consider if additional PM controls are warranted to control emissions of toxic metals. In that evaluation, the Agency will consider whether the additional controls, if any, should be promulgated in the future under the new Clean Air Act. See discussion in section III.A of Part One of this preamble. Finally, we note that permit writers also could impose a lower PM standard where facts warrant, pursuant to the omnibus permit authority in section 3005(c)(3).8

### A. Basis for Final Rule

Particulate matter (PM) is controlled from combustion sources to limit emissions of toxic metals and PM per se (i.e., because of human health and ecological impacts associated with PM that does not contain toxic metals). In the May 6, 1987 proposed rule, EPA suggested that a PM emission standard was not needed for boilers and industrial furnaces because the risk-based metals controls provide adequate control of metals emissions. The Agency reasoned that a standard intended to control PM per se would be more appropriately applied to these sources under authority of the Clean Air Act rather than RCRA.

EPA received numerous comments on the May 6, 1987 proposed rule suggesting the need for a particulate standard for boilers and furnaces burning hazardous waste. Many commenters believed that, notwithstanding the risk-based metals controls, unregulated PM emissions with adsorbed toxic metals and organic compounds could pose a significant health risk. In addition, three commenters suggested that EPA address the issue of particulate control during soot-blowing cycles when levels of particulate emissions are 4 to 7.2 times the level of emissions under normal operation. The Agency carefully considered these comments and subsequently determined that the risk-based metals standards should

EPA notes that permit writers choosing to invoke the omnibus permit authority of §270.32(b)(2) to add conditions to a RCRA permit must show that such conditions are necessary to ensure protection of human health and the environment and must provide support for the conditions to interested parties and accept and respond to comment. In addition, permit writers must justify in the administrative record supporting the permit any decisions based on omnibus authority.

be supplemented with a PM standard to provide a common measure of control for metals. This decision was based in part on a consideration of commenters' concerns about the limitations of risk-based metals standards. See 54 FR 43720-21. Hence, the Agency subsequently proposed a particulate emissions standard of 0.08 gr/dscf (grains/dry standard cubic foot) corrected to 7% oxygen in the October 26, 1989 supplement to the proposed rule. The standard would be applicable to all boilers and industrial furnaces not governed by a more stringent (NSPS or SIP) standard.

1. Alternatives Considered. In selecting the standard for boilers and industrial furnaces, the Agency considered the following alternatives:. (1) apply the current NSPS standard for steam generators burning waste; (2) apply the applicable NSPS; or (3) apply the existing hazardous waste incinerator standard. These options are discussed in the 1989 supplemental notice (54 FR 43720).

Many commenters supported the proposed particulate standard of 0.08 gr/dscf. Several commenters, however, opposed this limit, arguing against imposing a standard appropriate for incinerators on boilers and furnaces. Still other commenters suggested that the 0.08 gr/dscf limit did not go far enough in protecting the public health. These respondents argued for a lower limit comparable to that the Agency proposed for municipal waste incinerators.

The Agency continues to believe that the 0.08 gr/dscf PM standard, when used as a supplement to the risk-based metal controls provided by today's rule, provides substantial protection of human health and the environment.

2. Basis for Standard. Today's rule promulgates the proposed particulate emission limit of 0.08 gr/dscf because, as a supplement to the risk-based metals controls, it provides a common measure of protection from particulate emissions from boilers, industrial furnaces, and incinerators burning hazardous waste. In addition to providing control of particulate metals and adsorbed organic compounds, the 0.08 gr/dscf standard should also ensure that the Clean Air Act's National Ambient Air Quality Standard (NAAQS) for particulates is achieved in most cases. An analysis of existing sites shows that emissions of particulates at 0.08 gr/dscf could result in MEI levels of up to 30% of the maximum daily PM<sub>10</sub> (particulate matter under 10 microns) NAAQS (150 mg/m<sup>3</sup>). If background particulate levels at a site are high (i.e., the site is in a non-attainment area), particulate emissions from the device should also be addressed as part of the State Implementation Plan (SIP) (as they are now for hazardous waste incinerators in particulate non-attainment

areas). Therefore, although the 0.08 gr/dscf standard may not ensure compliance with the NAAQS in every situation, this issue will be addressed by the SIP since the facility would be, by definition, in a non-attainment area for particulate emissions.

## B. Interim Status Compliance Procedures

Facilities operating under interim status must comply with the PM emission standard. By the effective date of the rule, owners/operators must submit a certification of precompliance that documents their use of engineering judgment to show that, considering feed rates of ash from all feed streams, partitioning of ash to bottom ash or product, and the PM removal efficiency of the air pollution control system (APCS), PM emissions are not likely to exceed the 0.08 gr/dscf limit. Owners and operators must also establish and provide with the precompliance certification limits on feed rates of ash in all feed streams consistent with those used to determine that emissions of particulate matter are not likely to exceed the standard. The facility may not exceed these feed rates during interim status (unless amended by a revised certification of precompliance). Further, within 18 months (unless extended) of promulgation, owners/operators must conduct emissions testing and certify that emissions do not exceed the limit. See section VII in Part Three of this preamble for more information.

#### C. Implementation

Owners/operators must demonstrate compliance with the PM standard using Methods 1-5 of 40 CFR Part 60, Appendix A. The compliance test for certification during interim status and the trial burn for facilities applying for a RCRA operating permit must be representative of worst-case operating conditions with respect to particulate emissions that will occur during operation of the facility (i.e., because limits on operating conditions applicable for the remainder of interim status will be based on operating conditions during the compliance test).

The PM standard is implemented by limiting the feed rate of ash from all feed streams (i.e., hazardous waste, other fuels, raw materials) and by limits on APCS-specific operating parameters. The limits are established during interim status based on the compliance test, and in the operating permit based on the trial burn.

The final rule gives special consideration to cement and light-weight aggregate kilns because their raw material feed streams contain the vast majority of the ash input and resulting PM. Therefore, owners/operators of cement kilns and light-weight aggregate

kilns are not required to monitor ash feed rates of feedstreams. We emphasize, however, that cement kilns and lightweight aggregate kilns, like all BIFs, are still required to demonstrate conformance with the PM emission standard during a compliance test (under interim status) or trial burn (under a Part B application). The Agency believes that the capacity limit on the facility (expressed in appropriate units such as raw material feed rate) and the limits on the air pollution control system (APCS) operating parameters applicable during both interim status and under a subsequent operating permit will ensure that cement and light-weight kilns continuously comply with the PM standard 9

# II. Controls for Emissions of Toxic Organic Compounds

Burning hazardous waste that contains toxic organic compounds (i.e., organic compounds listed in Appendix VIII of 40 CFR Part 261) under poor combustion conditions can result in substantial emissions of the toxic compounds originally present in the waste as well as other compounds, due to partial but incomplete combustion of the constituents in the waste. The quantity of toxic organic compounds emitted depends on the concentrations of the toxic compounds in the waste, the waste firing rate (i.e., the percentage of total fuel provided by the hazardous waste to the boiler or industrial furnace), and the combustion conditions under which the waste is burned. The risk posed by the emissions depends on the quantity and toxicity of the compounds emitted and on the ambient levels to which persons are exposed. Hypothetical risk assessments show that under poor combustion conditions that achieve only 99 percent or 99.9 percent destruction and removal efficiency (DRE) of organic compounds, risks to the maximum exposed individual (MEI) from unburned carcinogenic organics found in hazardous waste can result in increased lifetime cancer risks of  $10^{-4}.10$ 

The Agency is controlling the emissions of toxic organic compounds from boilers and industrial furnaces that burn hazardous waste with two performance standards. First, a 99.99 percent destruction and removal efficiency (DRE) standard for principal organic hazardous constituents (POHCs) in waste feeds will ensure that constituents in the waste

We note, moreover, that some boilers and many industrial furnaces are already subject to a particulate matter (PM) standard under a NSPS, SIP, or PSD program and the applicable PM standard is generally more stringent than the 0.08 gr/dscf standard provided by today's rule. Thus, these devices are already under a regulatory compliance program for a PM standard. We note further that the more stringent PM standard applies.

Engineering-Science, <u>Background Information Document for the Development of Regulations to Control the Burning of Hazardous Waste in Boilers and Industrial Furnaces</u>, Volume III, January 1987 (NTIS # PB 87 173845).

are not emitted at levels that could pose significant risk in virtually all scenarios of which the Agency is aware. Second, limits on flue gas concentrations of carbon monoxide (CO) and, where specified, hydrocarbons (HC) will ensure that combustion devices operate continuously at high combustion efficiency and emit products of incomplete combustion (PICs) at levels that will not pose adverse effects on public health and the environment. The basis for these standards is discussed below.

#### A. DRE Standard

As proposed, the Agency is promulgating a 99.9999% DRE standard <sup>12</sup> for those acutely hazardous wastes listed because they contain dioxin <sup>13</sup> (and waste mixed with those wastes), and a 99.99 percent DRE performance standard for all other wastes. This standard is protective, it can be readily achieved by boilers and industrial furnaces, and it will ensure that the Agency's controls are consistent for all combustion devices (boilers, industrial furnaces, and incinerators) that pose similar risks.

Hypothetical risk assessments have shown that a 99.99 percent DRE standard for POHCs is protective of risks posed by emissions of organic constituents in the waste in virtually every scenario of which the Agency is aware. <sup>14</sup> (EPA considers elsewhere in this notice the issue of products of incomplete combustion.) Increased lifetime cancer risks to the maximum exposed individual (MEI) from an incinerator operating at 99.99 percent DRE would generally be 10<sup>-6</sup> or less. Threshold (i.e., noncarcinogenic) organic compounds also would not be expected to be present in emissions from hazardous waste burned in boilers and industrial furnaces at levels that could pose a health hazard under the 99.99 percent DRE standard.

EPA is aware, however, that the DRE standard does not directly control the mass emission rate (e.g., pounds per hour) of unburned toxic organic constituents in the waste. Although there are hypothetical situations in which risks from POHCs could be significant under a 99.99 percent DRE standard (e.g., boilers or industrial furnaces located in urban areas burning high volumes of waste with high concentrations of highly potent carcinogenic organics), the Agency is not aware that any such situations are actually

Except that 99.9999% DRE is required for dioxin-listed hazardous waste.

The proposed formula for calculating DRE has been revised in the final rule (see §266.104(a)) to make it mathematically correct considering use of significant figures.

EPA Hazardous Wastes FO20, FO21, FO22, FO23, FO26, and FO27.

Engineering Science, op. cit.

occurring. If, however, during the permit process, it appears that a high-risk scenario may exist, permit officials may use the omnibus permit authority 15 of Section 3005(c)(3) of the Resource Conservation and Recovery Act (RCRA) codified at §270.32(b)(2) to develop permit requirements, as necessary, to protect human health and the environment (e.g., by requiring a 99.9999 percent DRE, by limiting the feed rate of particular toxic compounds, or by setting a mass emissions rate).

1. Selection of POHCs for DRE Testing. In the April 27, 1990 proposed rule to amend the incinerator standards (55 FR 17890), EPA outlined the considerations to be made by applicants and permitting officials in selecting POHCs for DRE trial burns. Given that the DRE implementation procedures for boilers and industrial furnaces (BIFs) are identical to those for incinerators, the discussions in the incinerator proposed rule are pertinent to this rule.

A major factor in selecting a POHC for DRE testing is its incinerability relative to other toxic organic compounds. A number of indices can be used to predict incinerability including heat of combustion, autoignition temperature, thermal stability under excess oxygen conditions, and thermal stability under low oxygen (substoichiometric) conditions. An incinerability ranking based on thermal stability at low oxygen concentrations (TSLoO<sub>2</sub>) shows promise and is currently seeing widespread use in incinerator permits. A number of commenters responded to EPA's request for comment on the use of the TSLoO<sub>2</sub> index for POHC selection. In general, they raised no problems with use of the index. Their main concern appeared to be that EPA choose one index and apply it consistently.

The Agency, however, is not requiring the use of a particular index. Due to the various "failure modes" different organic compounds are susceptible to during the destruction process in a combustion device, and the evolving state of knowledge in this area, the Agency feels that the POHC selection process is technically complex, and that it should involve a number of considerations, rather than simply one incinerability ranking. Thus, EPA instead recommends that permit writers and applicants consider these indices and other relevant factors and use their judgment and applicable guidance on a case-by-case basis to select POHCs for the trial burn.

EPA notes that permit writers choosing to invoke the omnibus permit authority of §270.32(b)(2) to add conditions to a RCRA permit must show that such conditions are necessary to ensure protection of human health and the environment and must provide support for the conditions to interested parties and accept and respond to comment. In addition, permit writers must justify in the administrative record supporting the permit any decisions based on omnibus authority.

2. Use of POHC Surrogates. A number of laboratory-scale, pilot-scale, and field-scale tests have been conducted to investigate the use of nontoxic tracer surrogates (e.g., sulfur hexafluoride (SF<sub>6</sub>)) rather than POHCs selected from Appendix VIII of Part 261. Sulfur hexafluoride, in particular, shows promise as a conservative tracer surrogate for compounds which are susceptible to the thermal failure mode (i.e., it is difficult to destroy unless sufficiently high temperatures are reached). It is readily available commercially, and is inexpensive and nontoxic. POHCs that are listed on Appendix VIII, especially in situations where spiking is required to increase concentrations in a waste for DRE testing, are often difficult to obtain, are expensive, and are a health hazard to operators. Sampling and analysis techniques for SF<sub>6</sub> are well documented because of its long use as a tracer gas for monitoring ambient air and are more straightforward (simpler) and less expensive than sampling techniques for Appendix VIII, Part 261, compounds (e.g., VOST and MM5).

Numerous commenters responded to EPA's request for information on an approach for simplifying and standardizing DRE testing. Commenters supported standardization of DRE testing provided the approach is equitable for all boilers, industrial furnaces, and incinerators. Comments were received in support of all three approaches proposed by EPA ("POHC soup," surrogates, and specific waste analysis). Commenters generally supported use of surrogates in lieu of extensive waste analysis for design of DRE tests. Other commenters suggested using a limited number of major waste constituents as POHCs, such as carbon tetrachloride, perchloroethylene, trichloroethylene, and monochlorobenzene, until it can be shown that a universal surrogate, such as sulfur hexafluoride (SF<sub>6</sub>), is comparable in demonstrating DRE performance. Sulfur hexafluoride was recommended by some commenters as a good surrogate choice based on the high accuracy of results with the compound and ease of use.

However, since the April 27 proposed rule, data have become available showing cases where other organic compounds were more difficult to destroy than SF6 under conditions of low oxygen. This is consistent with theory, since SF6 can be destroyed under conditions of high temperature and low oxygen relatively easily compared to compounds which need oxygen to decompose. Thus, although SF6 appears to show promise as a surrogate for testing the thermal failure mode because of its stability at high temperatures, it does not appear to be adequate as a "universal" surrogate, since it does not test for low oxygen or "mixing" failure.

Nevertheless, today's rule explicitly allows the use of surrogate, nontoxic compounds for selection as POHCs for DRE testing. As for any other type of POHC, the use of such compounds must be approved on a case-by-case basis by permit officials based on technical support provided by the applicant. The applicant's trial burn plan must adequately document the correlation between the DRE of the surrogate compound and the DREs of the Appendix VIII compounds anticipated to be burned at the facility under the facility's permit.

3. Waiver of DRE Trial Burn for Boilers Operating Under the Special Operating Requirements In 1987, the Agency proposed to waive the trial burn requirement to demonstrate DREs for boilers that operate under special operating requirements (SOR). The SOR required that, in addition to meeting the proposed 100 ppmv CO limit, a qualifying boiler must: (1) burn at least 50 percent fossil fuel in the form of oil, gas, or coal; (2) operate at a load of at least 25 percent of its rated capacity; (3) burn hazardous waste fuel with an as-fired heating value of at least 8,000 Btu/lb; and (4) inject the hazardous waste fuel through an acceptable atomization firing system.

The SOR were based on the results of nonsteady-state boiler testing. From these results, the Agency believed that boilers operating under the SOR would maintain a hot, stable flame conducive to maintaining high combustion efficiency, resulting in maximum destruction of organic constituents in the hazardous waste fuel. The Agency believed that these boilers would achieve at least 99.99 percent DRE, and therefore, a trial burn to demonstrate DRE would not be necessary.

The Agency continues to believe that boilers operating under the SOR will achieve 99.99 percent DRE. However, based on comments received on the proposed SOR and on further examination of the previous steady-state and nonsteady-state boiler test results, the Agency has made the following modifications to the SOR:

- (1) limit eligibility for the waiver to nonstoker, watertube boilers;
- (2) revise the requirement that the boiler fire 50 percent fossil fuel or fuels derived from fossil fuel to include tall oil, to allow permit officials to approve on a case-by-case basis other nonhazardous fuels with combustion characteristics comparable to fossil fuel, and to require for all such primary fuels (i.e., fossil fuels, tall oil, and other fuels approved on a case-by-case basis) a minimum heating value of 8,000 Btu/lb;

- (3) clarify that the hazardous waste fuel fired must have an as-fired heating value of 8,000 Btu/lb and require that each fuel fired in the burner where hazardous waste is fired must have an as-fired heating value of 8,000 Btu/lb;
- (4) increase the minimum load requirement from 25% to 40%; and
- (5) eliminate the lower viscosity requirements for the hazardous waste and decrease the upper viscosity limits for the hazardous waste to 300 seconds, Saybolt Universal (SSU), measured at the as-fired temperature of the fuel.

As proposed in 1987, boilers with a trial burn waiver under the SOR must meet the Tier I CO limit of 100 ppmv<sup>16</sup> and must comply with all other requirements of the final rule (e.g., metals standards, PM limit).

The revised SOR are presented below, along with the basis for the revisions.

a. The Boiler Must Be a Nonstoker, Watertube Boiler. Commenters stated that the nonsteady-state testing of only three stoker and firetube boilers is insufficient to determine whether 99.99 percent DRE would always be achieved under the SOR. Commenters also maintained that the stoker and firetube boilers tested were not representative of all types and sizes.

The Agency agrees that there is limited data demonstrating that stoker and firetube boilers can achieve 99.99% DRE under the SOR. In the Agency's steady- and nonsteady-state testing, only three firetube boilers and one stoker boiler were tested under steady-state conditions, and one stoker boiler was tested under nonsteady-state conditions. The remainder of the boilers tested were watertube boilers.

The results from one of the firetube boiler tests generally support the ability of firetube boilers to achieve 99.99 percent DRE, but this boiler was specially designed to combust hazardous waste. The Agency is concerned whether more conventionally designed firetube boilers could easily achieve this level of DRE. DREs could not be calculated at one of the other firetube boiler tests due to inadequate waste feed levels, and sampling and analytical problems occurred at the third firetube boiler test. The stoker boiler tested under steady-state conditions did not demonstrate 99.99 percent DRE. In addition to the limited data for these boiler types, a greater potential exists for poor distribution of

Boilers complying with the Tier II PIC controls where CO levels exceed 100 ppmv are not eligible for the automatic waiver of the DRE trial burn. This is because the DRE test data used to support the waiver was obtained for boilers operating at CO levels below 100 ppmv.

combustion gases and localized cold spots in firetube and stoker boilers that can result in poor combustion conditions. This is because these boilers generally burn fuels with a large and variable particle size on a bed, thus, making even distribution of combustion air difficult. Therefore, the final rule precludes stoker or firetube boilers from the automatic waiver of a DRE trial burn.

b. A Minimum of 50 Percent of the Fuel fired to the Boiler Must Be High Quality "Primary" Fuel Consisting of Fossil Fuels or Fuels Derived From Fossil Fuels, Tall Oil, or, if Approved on a Case-By-Case Basis, Other Nonhazardous Fuel Comparable to Fossil Fuel, and All Such Primary Fuels Must Have a Minimum As-Fired Heating Value of 8,000 Btu/lb. Thirteen commenters found the 50 percent fossil fuel requirement to be overly restrictive. In particular, one commenter proposed that the requirement be rephrased to allow the burning of no more than 50 percent hazardous waste in mixtures such that nonhazardous waste fuel supplements can be fired. Another commenter suggested eliminating the fossil fuel requirement for wastes that have heating values comparable to fossil fuels. Eleven commenters supported the burning of high quality non-fossil fuels, such as tall oil (i.e., fuel derived from vegetable and rosin fatty acids) and the by-products derived from the fractional distillation of tall oil. Many of these commenters said they have burned these materials and claimed they have heating values and combustion characteristics similar to fossil fuels. Three commenters requested that the burning of wood wastes as a primary fuel be allowed. One of these commenters presented the results from six trial burns for wood waste boilers which demonstrated that combustion zone temperatures in these types of boilers are consistent, and that a hot, stable flame conducive to the destruction of organic constituents in the waste is present under these conditions.

Based on the comments and information presented regarding the use of tall oil (i.e., tall oil burns like commercial fuel oil), the Agency is revising the 50% primary fuel requirement to include tall oil. Also, the Agency believes that the combustion of other nonhazardous fuels that have heating values of at least 8,000 Btu/lb (representing the lower heating value range of most sub-bituminous coals), and combustion characteristics similar to fossil fuels, will ensure a hot, stable flame conducive to the destruction of organic constituents in the waste. An owner/operator who is planning to burn such a fuel supplement must present information on the supplement's combustion characteristics for the Director's review. Concerning wood wastes, the Agency continues to believe that these wastes may not provide the hot, stable combustion zone conditions needed to achieve 99.99 percent DRE. Due to the higher flue gas moisture, excess air, CO levels, and lower

furnace temperatures associated with wood firing, the potential for less than 99.99 percent DRE exists. Therefore, boilers that fire wood wastes must demonstrate DRE capabilities through a trial burn.

The 50 percent minimum primary fuel requirement, on a total heat or volume input basis, whichever results in the greater volume of primary fuel, also is needed to ensure appropriate combustion zone conditions. This limit was based on the maximum levels of hazardous waste burned in the boilers tested by EPA under nonsteady-state conditions.

Finally, the Agency recognized that the term "fossil fuel" can include peat or other fuels with heating values below 8,000 Btu/lb. Because the test data used to support the waiver were from boilers fired with primary fuels with heating values higher than 8,000 Btu/lb, the final rule applies the minimum 8,000 Btu/lb as-fired heating value limit to all fuels, including fossil fuels, used to meet the minimum 50% primary fuel requirement.

c. Boiler Load Must Be at Least 40 Percent. Several commenters addressed the proposed minimum load level of 25 percent. Only one commenter considered it to be too low. This commenter advocated an 80 percent load requirement unless high efficiency combustion can be demonstrated at the trial burn. One commenter considered the 25 percent requirement to be arbitrary, but within current practice. Another commenter recommended that the level be more flexible for multiple burner boilers. One commenter recommended that the requirement to maintain a boiler load of 25 percent be eliminated if the Btu value of the wastes burned is equivalent to that of coal thereby providing the heat input necessary to sustain normal combustion operations.

Boiler testing conducted at a load as low as 26 percent has demonstrated that certain boilers can achieve 99.99 percent DRE when operated at low loads. However, due to concerns related to flame stability, combustion control, and heat transfer effects associated with load turndown on some boilers, the Agency has raised the boiler load limit from 25 percent to 40 percent of design load. Operation of some boilers at loads of less than 40 percent can result in significantly higher excess air levels and localized decreases in flame temperatures. In addition, most of the boilers tested to develop the operating requirements operated at loads above 40%. Therefore, limiting the boiler load to 40% is more consistent with the available test data. If an owner/operator expects to operate a unit at a lower load while firing hazardous waste, a trial burn to demonstrate 99.99 percent DRE is required.

d. The Heating Value of the Hazardous Waste Fuel Must Be a Least 8,000 Btu/lb, As-Fired, and Each Fuel Fired in a Burner Where Hazardous Waste Is Fired Must Have a Heating Value of at Least 8,000 Btu/lb, As-Fired. Eleven commenters expressed concern that the "as-fired" requirement proposed in 1987 will require the blending of wastes that have heating values of less than 8,000 Btu/lb with other wastes and/or the primary fuel before atomization. Four commenters documented a number of problems with blending low Btu wastes, including immiscibility and other mixing problems, increased quantity of materials requiring handling, difficulty of controlling feed during unit upsets, and impracticality for coal-fired systems. Five commenters requested that the heating value be determined on a total-burner basis, as a composite of primary fuel and waste. Three additional commenters recommended that the minimum heating value of wastes be lowered to 5,000 Btu/lb.

The Agency agrees that waste fuel blending can present problems in some instances. However, the Agency is concerned that allowing low Btu wastes to be fired separately from the fuel and then atomized in the flame region of the burner might make it difficult to ensure good atomization, proper feed system operation, and, consequently, adequate combustion of the hazardous waste. Therefore, the 8,000 Btu/lb requirement, which represents the lower range of heating values of fossil fuels, applies to the as-fired heating value of the hazardous waste and to the as-fired heating value of any other fuel fired in the same burner with the hazardous waste.<sup>17</sup>

If hazardous waste with a heating value below 8,000 Btu/lb<sup>18</sup> is mixed with the "primary" fuel to meet the as-fired minimum heating value for hazardous waste of 8,000 Btu/lb, that quantity of primary fuel may not be counted toward the 50% primary fuel requirement. This is because the purpose of requiring 50% of the fuel to be "primary" fuel is to ensure a hot, stable flame to combust the hazardous waste. If a portion of the primary

We note that the 8,000 Btu/lb minimum heating value also applies to the "primary" fuel that must comprise at least 50% of the boiler's fuel requirements. However, the remainder of the boiler's fuel requirements may be provided by hazardous waste and other fuels. There are no restrictions on the other fuels unless they are fired in the same burner with the hazardous waste. In that case, those other fuels, like the hazardous waste and "primary" fuel, must have a minimum heating value of 8,000 Btu/lb.

We note that, as discussed elsewhere in the text, the sham recycling policy stays into effect until an existing facility certifies compliance with the emissions standards (see §6266.103(c)). Thus, until that time, hazardous waste burned in a BIF must have an asgenerated heating value of 5,000 Btu/lb, unless the waste is burned solely as an ingredient.

fuel is blended with the hazardous waste to increase the heating value of the hazardous waste as-fired, then that portion of the primary fuel is not providing the hot, stable flame.

The following example shows how this requirement will work. Suppose a boiler is fired with 70% primary fuel and 30% hazardous waste, and that half of the primary fuel is blended with the hazardous waste to achieve an as-fired heating value of 8,000 Btu/lb. This boiler would not be eligible for the automatic waiver of the DRE trial burn because it is fired with only 35% primary fuel (half of the 70%) that is not blended with the hazardous waste to meet the minimum as-fired heating value limit of 8,000 Btu/lb.

e. The Hazardous Waste Must Be Fired with an Atomization System. Seven commenters argued that lower viscosity limits are unnecessary. Three commenters stated that it is common to atomize wastes well below 150-200 SSU, and that No. 2 oil has a viscosity of 32.6-37.9 SSU at 100°F. One commenter indicated that the upper viscosity limits appear high for the atomization systems specified. One commenter disagreed and said that the high limits are in the correct range. Six commenters expressed concern that the particle size limits are overly restrictive. One commenter stated that diverse waste streams can be handled to achieve good destruction without particle size limits. Another commenter disagreed with EPA by stating that they are not familiar with nozzles designed for particle sizes as small as 200 mesh. Three commenters said the waste viscosity should be left to the discretion of the owner/operator since it is industry practice to operate at viscosities which provide optimum atomization.

Based on the commenters' arguments, the Agency has eliminated the lower viscosity requirements and reduced the upper limit to 300 SSU (Seconds, Saybolt Universal) measured at the as-fired temperature of the hazardous waste. We eliminated the lower level because, after consideration of comments and re-evaluation, we believe that the concern stated at proposal — formation of a fog at low viscosity levels which could result in poor combustion conditions — is not likely to occur. At proposal, the Agency established upper viscosity limits ranging from 300 to 5,000 SSU, depending on the type of atomization system. Commenters noted that, as a practical matter, wastes with as-fired viscosities greater than 300 are not fired in an atomization system. These modifications will give facilities the flexibility to preheat wastes before atomization and are consistent with general industry practice for good atomization.

Regarding particle size limits the final rule establishes the proposed limits. When high pressure air or steam atomizers, low pressure atomizers, or mechanical atomizers,

70% of the waste must pass a 200 mesh (74 micron) screen. When a rotary cup atomizer is used, 70% of the waste must pass a 100 mesh (150 micron) screen. These mesh sizes are consistent with the design droplet size of the atomizers.

Owners/operators of boilers who propose to fire hazardous waste outside these viscosity and particle size limits must conduct a DRE trial burn.

#### B. PIC Controls.

The burning of hazardous waste, like virtually any combustion process, results in emissions of incompletely burned organic compounds, or products of incomplete combustion (PICs). PICs can be unburned organic compounds that were present in the waste, thermal decomposition products resulting from organic constituents in the waste, or compounds synthesized during or immediately after combustion. If a device is operated under poor combustion conditions, substantial emissions of PICs can result (even if 99.99% DRE is demonstrated for POHCs; this just means that the POHC is not being emitted in its original form). However, it should be noted that estimates of risk to public health resulting from PICs, based on available emissions data, indicate that PIC emissions do not pose significant risks when BIFs and incinerators are operated under good combustion conditions.

Nonetheless, the Agency is concerned about the potential health risk from PICs because the available information has serious limitations. It is very difficult to identify and quantify emissions of thousands of different compounds, some of which are present in minute quantities. Although elaborate and expensive sampling and analytical techniques have been developed that can identify many PICs, many others cannot be identified and quantified with current techniques. Further, health effects information adequate to conduct a health risk assessment considering exposure via direct inhalation is not currently available on many organic compounds that may be emitted from combustion systems. Finally, the available public health and environmental risk assessment tools are incomplete. Data are currently available to conduct indirect exposure analyses (e.g., exposure via the food chain, drinking water, dermal exposure) on only a few organic compounds, and it will be some time before the Agency will be able to quantify impacts on ecological resources on a site-specific basis for purposes of establishing emissions standards.

Given the limited information about the hazards that PIC emissions may pose, EPA believes it is prudent to require that boilers and industrial furnaces operate at a high combustion efficiency to minimize PIC emissions.

EPA is promulgating today a two-tiered approach to control PICs as discussed in the October 29, 1989, supplemental notice (54 FR 43721-28). Under Tier I, CO is limited to 100 ppmv. Under Tier II, the Agency is providing an alternative standard. The facility need not meet the 100 ppmv CO limit provided the facility can demonstrate that the hydrocarbon (HC) concentration in the stack gas does not exceed a good operating practice-based limit of 20 ppmv. The alternative CO limit under Tier II must be established during the test burn based on the average over all runs of the highest hourly rolling average for each run.

1. Use of a CO Limit to Control PICs. Generally accepted combustion theory holds that low CO flue gas levels combined with low excess oxygen levels indicate a boiler, industrial furnace, or incinerator is operating at high combustion efficiency. Operating under high combustion efficiency helps to ensure minimum emissions of unburned (or incompletely burned) organics. In the first stage of the combustion of hazardous waste fuel, the POHCs thermally decompose in the flame to form other, usually smaller, compounds termed products of incomplete combustion. In this first stage of combustion, these PICs also decompose to form CO.

The second stage of combustion involves the oxidation of CO to CO<sub>2</sub> (carbon dioxide). The CO to CO<sub>2</sub> step is the slowest (rate-controlling) step in the combustion process because CO is considered to be more thermally stable (difficult to oxidize) than other intermediate products of the combustion of hazardous waste constituents. Because fuel is being fired continuously, these combustion stages occur simultaneously.

Thus, in the waste combustion process, the "destruction" of POHCs is independent of flue gas CO levels. CO flue gas levels cannot be correlated with DREs for POHCs, and may also not correlate well with PIC destruction. Although some emissions data indicate a weak correlation between CO and PICs, the data generally indicate that there is a relationship between the two parameters: when CO is low, PIC emissions are relatively low. The converse may not hold: when CO is high, PICs may or may not be high.

Low CO is an indicator of the status of the CO to CO<sub>2</sub> conversion process, the last rate-limiting oxidation process. Because oxidation of CO to CO<sub>2</sub> occurs after the

destruction of a POHC and its (other) intermediates (PICs), the absence of CO is a useful indication of POHC and PIC destruction. The presence of high levels of CO in the flue gas is a useful indication of inefficient combustion, and at some level of elevated CO flue gas concentration, is an indication of the failure of the PIC and POHC destruction process.

EPA believes it is necessary to limit CO levels to levels that are indicative of high combustion efficiency because the precise CO level that indicates significant failure of the PIC and POHC destruction process is not known. In fact, this critical CO level may depend on site-specific and event-specific factors (e.g., fuel type, fuel mix, air-to-fuel ratios, and the rate and extent of changes in these and other factors that affect combustion efficiency). EPA believes that limiting CO levels is also reasonable because: (1) it is a widely practiced approach for monitoring combustion efficiency - some boilers and industrial furnaces are already equipped with CO monitors, and many are equipped with flue gas oxygen monitors; (2) the monitors may pay for themselves through fuel savings resulting from operation of the boiler or industrial furnace closer to maximum combustion efficiency; and (3) well-designed and well-operated boilers and industrial furnaces can readily be operated in conformance with either the 100 ppmv CO limit under Tier I, or the 20 ppmv HC limit under Tier II.

## 2. Tier I PIC Controls: 100 ppmv CO Limit.

a. Basis for the 100 ppmv CO Limit. The May 6, 1987 proposed rule would have applied the same CO emission limits to all boilers and industrial furnaces: a lower limit of 100 ppmv over an hourly rolling average and a 500 ppmv limit over a 10-minute rolling average. The hazardous waste feed would be shut off automatically if either limit was exceeded. However, the hazardous waste would be cutoff immediately once the 500 ppmv limit was exceeded while the waste feed would be cutoff within 10 minutes if the 100 ppmv limit was exceeded. Further if the hazardous waste feed was cutoff more than 10 times in a month, the proposed rule would have prohibited further hazardous waste burning pending review and approval by enforcement officials. The lower limit of 100 ppmv was selected as representative of steady-state high efficiency combustion conditions resulting in PIC emissions that would not pose a significant risk. The higher limit of 500 ppmv was proposed to limit the frequency of emission spikes that inevitably accompany routine operational "upsets," such as load changes and start-ups of waste firing.

While two commenters stated that the proposed 100 ppmv CO limit is arbitrary, six commenters supported the Tier I CO limit of 100 ppmv. One commenter supported both

the 100 ppmv CO limit over an hourly rolling average, and the 500 ppmv CO limit over a 10-minute rolling average. Three additional commenters also expressed support for the 500 ppmv CO limit over a 10-minute rolling average. Three other commenters supported a 500 ppmv CO limit over an hourly rolling average, and stated that a maximum 1,000 ppmv CO limit can be included in addition to a 10-minute average.

Many commenters opposed the CO trigger limits and associated limits on the number of waste feed cutoffs proposed in May 1987. Primarily, commenters objected to one set of CO emission limits as applicable to all boilers and industrial furnaces. Further, they argued that PIC emissions will not be significant if, when the waste feed is cutoff, the combustion chamber temperatures are maintained while the waste remains in the chamber. Six commenters argued that the trigger limits will result in increased NO<sub>x</sub> emissions. One commenter stated that NO<sub>x</sub> and CO cannot be lowered simultaneously, and added that many low NO<sub>x</sub> boilers may not be able to meet these CO limits. As an alternative, one commenter stated that a higher Tier I CO limit should be allowed for less toxic emissions; however, this commenter did not provide an alternative approach for identifying the toxicity of emissions. One commenter suggested that EPA retain two alternatives to the CO standard: establishing an alternative standard based on nonmethane, ethane hydrocarbon (NMEHC) emissions, and a case-by-case risk assessment approach.

As a result of these and other comments and further evaluation, EPA is promulgating the Tier I limits based on a maximum hourly rolling average CO limit of 100 ppmv, corrected to 7 percent flue gas oxygen content. If this limit is exceeded, the hazardous waste feed must be automatically and immediately cutoff. The final rule does not restrict the number of waste feed cutoffs because: (1) combustion chamber temperatures must be maintained after a cutoff; and (2) the number of cutoffs will be minimized by allowing CO concentrations to be averaged over a 60-minute period (i.e., the hourly rolling average) and by the recommended use of pre-alarms to provide time to remedy the problem or to allow a staged waste cutoff before reaching the CO limit. Nonetheless, the Agency retains the authority to limit the frequency of cutoffs as the facts warrant. See §266.103(e)(7)(ii). The final rule does not include the proposed 500 ppmv rolling average over a 10-minute limit on CO because we do not believe it is needed given that the final rule requires immediate waste feed cutoff when the 100 ppmv hourly rolling average limit is exceeded. In addition, several commenters argued that the 500 ppmv limit was arbitrary.

In addition, EPA is promulgating alternative (Tier II) standards (discussed below), as discussed in the October 1989 supplemental notice, for control of PIC emissions from boilers and industrial furnaces. The Agency believes that the alternative controls will allow facilities flexibility in meeting both the PIC controls and NO<sub>X</sub> emissions standards (imposed under different regulatory authorities) simultaneously. The Agency believes that the alternative, Tier II standards for control of PIC emissions are needed to address issues and concerns raised by commenters on the proposed rule.

The 100 ppmv CO limit promulgated today for Tier I is indicative of steady-state (i.e., normal), efficient combustion conditions. The time-weighted average for the CO limit is provided to accommodate the CO spikes that inevitably occur during routine "upsets," such as when hazardous waste fuel firing starts, when there is a load change on an industrial boiler, or when the composition of fuels varies. Given that CO is a sensitive indicator of overall combustion conditions, and that it may be a conservative indicator of POHC and PIC destruction, EPA is implementing CO control limits based on timeweighted averages of exceedances rather than implementing fixed CO limits. Fixed limits that do not acknowledge inevitable CO spikes and that do not give owners and operators time to adjust combustion conditions actually could result in greater emissions of PICs because each time hazardous waste firing is interrupted, CO concentrations increase, and emissions of incompletely burned organics may also increase. (Note, however, that there is a requirement to maintain combustion chamber temperature after a waste feed cutoff while waste remains in the chamber that is intended to minimize HC emissions after a cutoff.) Thus, any controls on CO must balance the effects of organic emissions that may result from overly stringent CO limits that require frequent waste feed interruptions with the effects of emissions resulting from less stringent controls that acknowledge inevitable CO spikes.

The Agency has considered whether the 100 ppmv CO limit is, in fact, too stringent given that we acknowledge the limit was chosen from within the range of reasonable values that may be considered indicative of good combustion conditions -- 50 to 250 ppmv. We attempted to obtain CO/time profiles from a number of well-operated devices to determine the percentage of time the facilities operated within particular CO ranges. <sup>19</sup> We thought to use this data to predict the frequency of waste feed cutoffs that would be required at various

<sup>19</sup> Energy and Environmental Research Corporation, "Guidance on Metal and PIC Emissions from Hazardous Waste Incinerators", Final Report, September 21, 1990.

CO limits. Unfortunately, the analyses could not be conducted because the facilities we evaluated were operating under specific CO limits and their CO levels never exceeded those limits when burning hazardous waste. We found that the facilities learned to comply with the CO limits they had to meet.

Moreover, we believe that the 100 ppmv CO limit is reasonable for a number of reasons. Not only is it within the range of CO levels that are indicative of good combustion conditions, but the Agency believes that it is not too low because: (1) it is higher than the technology-based 50 ppmv CO level EPA requires for boilers burning waste PCBs (see 40 CFR Part 761); (2) it is higher than the CO limits included in many hazardous waste incinerator permits<sup>20</sup>; (3) the Agency explicitly encourages the use of pre-alarms to minimize the frequency of automatic waste feed cutoffs<sup>21</sup>; and (4) the limit is implemented on an hourly rolling average basis which allows and minimizes the effects of short-term CO spikes.

We also note that the Agency may soon promulgate regulations for municipal waste combustors (MWCs) that, among other controls, may limit CO concentrations to 50, 100, or 150 ppmv (as proposed), depending on the type of MWC, over a four hour rolling average and dry-corrected to 7% oxygen. The MWC limits are technology-based -- they represent levels readily achievable by well-designed and well-operated units. EPA does not believe that the MWC limits present a conflict with the 100 ppmv (with provisions for an alternative higher limit if HC concentrations are less than 20 ppmv) limit for BIFs under today's rule. The Agency is confident that the BIF rule is protective because the Agency has determined that, when CO levels are less than 100 ppmv, PIC emissions do not pose significant risk. Thus, although the 100 ppmv limit is not a best demonstrated technology-based limit (many BIFs (and hazardous waste incinerators) readily operate at CO levels well below 100 ppmv), the 100 ppmv CO limit will ensure protection of human health and the environment.

As stated above, the CO limits are based on a flue gas oxygen content of 7 percent. One commenter indicated that EPA's reasoning for using the CO correction of 7 percent

We note that the Agency proposed on April 27, 1990 to apply to hazardous waste incinerators the same CO/HC limits that today's rule applies to BIFs.

If the CO limit is "too low" for a given facility's design and operating conditions, then frequent waste feed cutoffs may occur. Frequent waste feed cutoffs may actually increase PIC emissions because the resulting perturbation to the combustion system may upset the temperature, oxygen, fuel relationships needed for complete combustion.

oxygen is not clear. The commenter believes the 7 percent correction factor is unfair for thermal units which, under normal conditions, need to operate at oxygen levels greater than 7 percent, yet operate with low levels of CO and HCs. EPA believes that correcting CO levels for flue gas oxygen content is necessary because without this correction, high CO flue gas concentrations could be diluted by high rates of excess oxygen. In today's rule, EPA is requiring that CO be corrected to a flue gas oxygen content of 7 percent because the majority of boilers and industrial furnaces achieve high combustion efficiency at optimum flue gas oxygen levels ranging from 3 percent to 10 percent. The optimum oxygen level to achieve high combustion efficiency for a given device will vary depending on factors such as fuel mix and boiler load. In general, large combustion devices (in terms of heat input capacity) have optimum oxygen requirements on the low end of the range of oxygen content, while smaller units require higher oxygen levels. EPA believes that a correction level of 7 percent is reasonable since this oxygen level is in the middle of the range of typical operation for all devices and since the majority of devices burning hazardous waste fuels have moderate heat input capacities (e.g., 20-150 MM Btu/hr). In addition, 7 percent oxygen is the reference level for the existing particulate standard for hazardous waste incinerators under 40 CFR 264.343(c).

Moreover, the oxygen level to which CO values are corrected is not significant since the CO levels for all facilities are corrected to a common basis. If the oxygen correction level were changed from 7% to some other value, then theoretically, the CO limit would have to be adjusted accordingly, and the effect on individual facilities would remain the same.

b. Implementation of the 100 ppmv CO Limit. The procedures used to implement the 100 ppmv CO limit are discussed below, including oxygen and moisture correction, format of the limit, and compliance with the limit.

Oxygen and Moisture Correction. The CO limit under Tier I (and Tier II) is on a dry gas basis corrected to 7 percent oxygen. The oxygen correction normalizes the CO data to a common base, accounting for the variation in design and operation of the various combustion devices. In-system leakage, facility size, and waste feed type are other factors that cause oxygen concentrations to vary widely in flue gases and were considered in selection of the oxygen correction factor. The correction for moisture normalizes the CO data that results from the different types of CO monitors used at facilities (e.g., extractive, in situ, etc.). EPA's evaluation indicates that application of the oxygen and moisture corrections can change measured CO levels by a factor of two in some cases.

Measured CO levels must be corrected continuously for the amount of oxygen in the stack gas according to the formula:

$$CO_c = CO_m \times 14/(E-Y)$$

where CO<sub>C</sub> is the corrected concentration of CO in the stack gas, CO<sub>m</sub> is the measured CO concentration according to guidelines specified in Appendix 2.1 provided in Methods Manual for Compliance with the BIF Regulations (Methods Manual)<sup>22</sup>, E is the percentage of oxygen contained in the air used for combustion, and Y is the measured oxygen concentration on a dry basis in the stack. Oxygen must be measured at the same stack location at which CO is measured under procedures that are also provided in Appendix 2.1 of the Methods Manual.

Format of the CO Limit. EPA proposed that the CO limits be implemented under either of two alternative formats, the hourly rolling average format or the time-above-a-limit format. Under this approach, applicants would select the preferred approach on a case-by-case basis. Comments were received in support of both alternative formats. Based on further evaluation of the two formats and for reasons explained below, EPA is requiring use of the hourly rolling average format for compliance with this rule.

Under the hourly rolling average format, a facility must measure and record CO levels as an hourly rolling average. This approach allows instantaneous CO peaks without requiring a cutoff provided that at other times during the previous hour CO levels were correspondingly below the limit. This approach requires a CO monitoring system that can continuously measure and adjust the oxygen correction factor and compute the hourly rolling averages.

Under the proposed time-above-a-limit format, dual CO limits would be established in the permit: the first as a never-to-exceed limit and the second as a lower limit for cumulative exceedances of no more than a specified period of time in an hour. These limits and the time duration of the exceedances would be established on a case-by-case basis by equating the mass emissions (peak areas) in both the formats (time-above-a-limit and hourly rolling average formats) so that the regulation would be equally stringent in both cases. The instruments needed for the time-above-a-limit format would include a CO

U.S. EPA, Methods Manual for Compliance with the BIF Regulations, December 1990. Available from the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161, (703) 487-4600. The document number is PB 91-120-006.

monitor, a recorder, and a timer that could indicate the cumulative time of exceedances in every clock hour, at the end of which it would be recalibrated (manually or electronically). Oxygen would not be measured continuously in this format; instead an oxygen correction factor would be determined from operating data collected during the trial burn. Subsequently, oxygen correction factors would be determined annually or at more frequent intervals specified in the facility permit.

EPA has re-examined the time-above-the-limit format in light of several comments received and has decided to delete this alternative in today's final rule because:.

- 1. Since a facility would not be required to measure oxygen continuously under this format, there would be no assurance that a facility would be operated reasonably close to the oxygen level at which it operated during the trial burn. Even with a daily determination of an oxygen correction factor, there would be the possibility of "gaming" by the facility (operating the facility at low oxygen levels during the short test period when the oxygen is measured, getting a favorable correction factor established on that basis, and thereafter letting the facility operate at high oxygen levels). Since the major advantage of this format was the cheaper cost due to the omission of the oxygen monitoring requirement, adding continuous oxygen monitoring to this format would remove this advantage as well; and
- 2. The proposed computations for converting hourly rolling averages to this format would be cumbersome, inexact, and above all, very restrictive. To obtain a conservative conversion, a permit writer would have to assume that CO levels will remain at the established never-to-exceed limit for the full specified time in the hour, and at the lower established limit the rest of the time. The CO limits obtained by these computations would be very restrictive. As an example, a conversion of a Tier I limit of 100 ppmv hourly rolling average for a facility having a single CO excursion of 4-minutes duration in which the peak level was 1,000 ppmv, would result in a permit specifying that for the remaining 56 minutes, CO could not exceed 34 ppmv, a very restrictive limit. For example, a CO profile of 30 ppmv for 55 minutes and 40 ppmv for the remaining 5 minutes would result in a violation.

Compliance with the Tier I CO Limit. The Agency considered a number of alternative approaches for evaluating CO readings during trial burns to determine compliance with the 100 ppmv limit, including: (1) the time-weighted average (or the average of the hourly rolling averages); (2) the average of the highest hourly rolling average. The time-weighted average alternative provides the lowest CO level that could reasonably be used to determine compliance, and the highest hourly rolling average alternative provides the highest CO level that could reasonably be used. EPA is requiring the use of the most conservative of these approaches, the highest hourly rolling average approach, for interpreting trial burn CO emissions for compliance with the 100 ppmv Tier I limit. (This approach is conservative because trial burn CO levels are compared to the maximum CO

allowed under Tier I - 100 ppmv.) EPA believes this conservative approach is reasonable since compliance with the Tier I CO limit allows applicants to avoid the Tier II requirement of evaluating HC emissions to provide the additional assurance (or confirmation) that HC emissions do not exceed levels representative of good operating practice.

- 3. Tier II PIC Controls: Limits on CO and HC.
- a. Need for Tier II PIC Controls. Commenters indicated that several types of boilers and many cement kilns will not be able to meet the (Tier I) 100 ppmv CO limit proposed in May 1987 even though HC concentrations will not be high at elevated CO levels. For example, boilers that burn residual oil or coal typically operate with CO emission levels above the Tier I 100 ppmv CO limit because of inherent fuel combustion characteristics, equipment design constraints, routine transient combustion-related events, requirements for multiple fuel flexibility, and requirements for compliance with NO<sub>X</sub> emission standards established under the Clean Air Act. Attempts to reduce CO emissions from these devices to meet the Tier I limit could prove unsuccessful. In addition, there is a possibility that thermal efficiency could be adversely affected if these attempts are successful.

Similarly, industry and trade groups for the cement industry voiced strong opposition to the 100 ppmv CO limit for cement kilns. These commenters indicated that some cement kilns, especially modern precalciners, routinely emit CO above the Tier I 100 ppmv limit. In general, commenters indicated that while the Tier I limit may be appropriate for combustion devices in which only fuel (fossil or hazardous waste) enters the combustion chamber, it is inappropriate for cement kilns and other product kilns in which massive amounts of feedstocks are processed. These feedstocks can generate large quantities of CO emissions which are unrelated to the combustion efficiency of burning the waste and fuel. Whereas all the CO from boilers and some industrial furnaces is combustion-generated, the bulk of the CO from product kilns can be the result of process events unrelated to the combustion conditions at the burner where wastes are introduced.<sup>23</sup> Therefore, limiting CO emissions from these combustion devices to the Tier I 100 ppmv level may be difficult and may not be warranted as a means of minimizing risk from PICs.

For example, CO can be generated from the trace levels of organic matter contained in the raw materials as the materials move down the kiln from the "cold" feed end to the "hot" end where the fuel and waste is fired and the product is discharged.

In summary, commenters argued that there are specific instances and classes of combustion devices for which the Tier I CO limit would be difficult or virtually impossible to meet, and thus this limit is inappropriate since EPA has not established a direct correlation between CO emissions, PIC emissions, and health risks.

In light of these concerns, commenters suggested that EPA establish CO limits for specific categories of combustion devices based on CO levels achieved by units operating under best operating practices (BOP). The Agency considered this approach but determined that equipment-specific CO trigger limits would be difficult to establish and support and would not necessarily provide adequate protection from PIC emissions. Nonetheless, EPA believes that the CO limits should be flexible to avoid major economic impacts on the regulated community since no direct correlation has been established between exceeding the 100 ppmv CO limit and increasing health risks from PIC emissions. EPA believes, however, that at some elevated CO level PIC emissions would pose significant risk. At this time, EPA is unable to identify a precise CO trigger level since the trigger level may vary by the type and design of the combustion device and the fuel mix used in the device. Consequently, EPA has established a two-tiered approach to control PICs. Under Tier I, CO is limited to 100 ppmv or less, as discussed above. Under Tier II, CO levels can exceed 100 ppmv provided that the owner or operator demonstrate that the HC concentration in the stack gas does not exceed a good operating practice-based limit of 20 ppmv (except that the Director may establish under §266.104(f) an alternative HC limit for furnaces that feed raw material containing organic matter and, thus, cannot meet the 20 ppmv limit).

Under Tier II, the CO limit for a facility is based on the levels achieved during a successful compliance test. The Agency originally proposed two alternative approaches for establishing HC emission limits under the Tier II waiver: a health-based approach and a technology-based approach. These two alternatives and EPA's rationale for selecting the technology-based approach for the final rule are discussed below. Before moving to those discussions, however, it may be useful to summarize the conclusions of an evaluation by EPA's Science Advisory Board of the proposed PIC controls.

- b. Comments by EPA's Science Advisory Board (SAB). We present below a summary of SAB's conclusions<sup>24</sup> on the scientific support for EPA's proposed PIC controls and EPA's response:
  - SAB: The Agency has not documented that PICs from hazardous waste combustion can cause significant health risk to human health or the environment.
    - EPA Response: While the Agency agrees that available data do not show that PICs are likely to pose a significant health risk, EPA's emissions testing to date has been able to identify and quantify only as much as 60% of the organic compounds being emitted during any test. During many of EPA's tests, less than 5 to 10% of organic emissions were characterized. The Agency is concerned that this large fraction of uncharacterized organic emissions could be comprised of compounds that can pose significant health risk. Therefore, the Agency believes that PICs have the potential to present a hazard and should be controlled.
  - SAB: It is prudent to control PICs given the inability to show that they do not pose a health risk because of limitations of sampling and analytical techniques and health and environmental impact assessment data and methodologies.
    - EPA Response: The Agency agrees. Additional emissions testing cannot be used to determine if, in fact, PICs can pose significant risk because the sampling and analytical techniques are not available to identify the unknown compounds. Moreover, even if the techniques were available, health effects data are not likely to be available for the compounds so that a risk assessment could not be conducted.
  - SAB: The use of CO and HC to ensure high combustion efficiency seems to be a reasonable approach to control PIC emissions.
    - EPA Response: The Agency agrees.
  - SAB: Under the Tier II controls when CO exceeds 100 ppmv, HC should be monitored continuously.

U.S. EPA, "Report of the Products of Incomplete Combustion Subcommittee of the Science Advisory Board", Report # EPA-SAB-EC-90-004, January 1990.

- EPA Response: The Agency agrees. Today's final rule requires continuous HC monitoring under the Tier II controls (see §266.104(c)) when CO levels exceed 100 ppmv, and for certain industrial furnaces irrespective of CO level (see §§266.104(d) for permitted furnaces and 266.103(a)(5) for furnaces operating under interim status).
- SAB: There is no scientific support for the health-based approach to establish HC limits on a site-specific basis based on a calculated "unit risk" value for total HC and stack gas monitoring of HC concentrations.
  - EPA Response: The final rule does not allow the use of the proposed health-based approach to control HC. HC are controlled under the technology-based limit of 20 ppmv. See §266.105(c).
- SAB: The risk assessment procedures are adequate, however, to show that the technology-based HC limit of 20 ppmv appears to be protective of human health.
  - EPA Response: The Agency agrees.
- SAB: The Agency should show that the proposed limits for CO and HC do not result in frequent automatic waste feed cutoffs that may increase PIC emissions.
  - EPA Response: See discussion in section C.2.b.i above.

Thus, the SAB supported the overall reasonableness of the course adopted in this rule to control potential risks from emissions of PICs.

c. Health-Based Approach for HC Limits. Under the Tier II health-based approach, the Agency proposed to allow applicants to demonstrate that PIC emissions from combustion devices pose an acceptable risk (i.e., less than  $10^{-5}$ ) to the maximum exposed individual (MEI). Under this approach, EPA proposed to require that applicants quantify HC emissions during trial burns and assume that all hydrocarbons are carcinogenic compounds with a unit risk value that would be calculated based on available data. The HC unit risk value would be  $1.0 \times 10^{-5}$  m<sup>3</sup>/ug and would represent the adjusted 95th percentile weighted (i.e., by emission concentration) average unit risk of all the hydrocarbon emission data in EPA's database of field testing of boilers, industrial furnaces, and incinerators burning hazardous waste. The weighted unit risk value for HC considers emissions data for carcinogenic PICs (e.g., chlorinated dioxins and furans, benzene,

chloroform, and carbon tetrachloride) as well as data for PICs that are not suspected carcinogens and are considered to be relatively nontoxic (e.g., methane, and other C1 as well as C2 hydrocarbons).<sup>25</sup>

The Agency proposed to implement this provision by back-calculating an acceptable HC emission rate (and, based on stack gas flow rates, a HC concentration) from the acceptable ambient level based on the calculated "total HC" unit risk value discussed above and allowing an incremental cancer risk of 1 in 100,000.

A number of commenters supported the health-based approach while several others pointed out that the approach was seriously flawed. EPA's Science Advisory Board reviewed the approach as discussed above and concluded that the site-specific, health-based approach of controlling HC was not scientifically supportable.

Upon re-evaluation, EPA believes that basing the HC limit on a health-based approach is not supportable and, thus, has not selected this approach for the final rule. Given the limited data base on the types and concentrations of PICs emitted over a range of operating conditions, we are concerned that the potency value that the proposed approach would apply to the total mass of hydrocarbons emitted may not be appropriate. It is not clear whether the proposed potency value may overstate or understate the risk posed by HC emissions. In addition, we are concerned that we do not fully understand what types of hydrocarbon emissions are actually detected by the continuous monitoring equipment. For example, as we discussed at proposal, certain halogenated compounds are under reported by the HC detection system. Finally, as we noted at proposal, the proposed risk-based approach could allow extremely high HC concentrations -- concentrations clearly indicative of combustion upset conditions.

d. Technology-Based Approach: 20 ppmv HC Limit. Under the technology-based approach, the Tier I CO limit of 100 ppmv will not have to be met if HC levels in the stack gas do not exceed a good operating practice-based limit of 20 ppmv<sup>26</sup> (measured on an hourly rolling average basis, reported as propane, dry corrected to 7% oxygen). As noted

Additional information on the development of the unit risk factor can be found in U.S. EPA, <u>Background Information Document for the Development of Regulations for PIC Emissions from Hazardous Waste Incinerators</u>, October 1989.

As discussed at proposal, the 20 ppmv limit represents a demarcation between good and poor combustion conditions based on HC emissions data from 24 facilities. The 20 ppmv limit is not based on best operating practice. A <u>best</u> operating practice limit would be set a level on the order of 5 ppmv.

above, EPA developed this technology-based approach because of current scientific concerns (seconded by the SAB) related to a health-based approach. In addition, the health-based approach could allow HC levels of several hundred ppmv, levels that are clearly indicative of "upset" combustion conditions. The approach, as noted above, lacks a firm scientific basis and could allow facilities to operate under upset conditions. EPA would not authorize such operations unless reasonably certain they would not pose a significant risk to human health and the environment. Such reasonable certainty does not exist here.

One commenter agreed that the PIC standard should be protective without imposing a technology "fix." Although EPA believes the development of a health-based approach is a step in the right direction, the Agency is concerned about whether the health-based Tier II approach is adequately protective given the limited database on PIC emissions and the uncertainty as to what fraction of organic emissions would be detected by the HC monitoring system. Despite the limitations of the HC health risk assessment methodology, EPA believes (and the SAB concurs) it is reasonable to use this methodology to predict whether a technology-based limit appears to be protective. Accordingly, EPA used the health risk assessment methodology to show that a 20 ppmv HC limit would not result in an incremental lifetime cancer risk to the hypothetical maximum exposed individual greater than 1 in 100,000...

The final rule establishes limits for both CO and HC under the Tier II PIC controls. The CO limit is established as the average over all runs of the highest hourly rolling average for each run of the compliance test or trial burn. To demonstrate compliance with the HC limit, the highest hourly rolling average HC level during the compliance test or trial burn cannot exceed 20 ppmv (except as otherwise provided for furnaces feeding raw materials containing organic matter), reported as propane, corrected to 7% oxygen on a dry basis.

The Agency considered whether to establish provision for a case-by-case waiver of the 20 ppmv HC limit based either on health-risk assessment or technical feasibility (i.e., feasibility of providing combustion conditions to minimize fuel-generated HC). The final rule does not provide for a waiver of the 20 ppmv HC limit as an indicator of good combustion conditions and minimum fuel-generated PIC emissions. (The final rule does, however, allow the Director to establish under the Part B permit proceedings an alternative HC limit for industrial furnaces (e.g., cement kilns, light-weight aggregate kilns) to account for hydrocarbons that are emitted from trace levels of organic matter in the raw material. Any alternative HC limit established for a furnace will ensure that fuel-generated

hydrocarbons (hazardous waste and other fuels) are less than 20 ppmv by establishing the HC limit based on HC concentrations when the system is designed and operated under good combustion conditions without burning hazardous waste.<sup>27</sup> See section II.B.5 of Part Three of this preamble for more discussion of the alternative HC limit for industrial furnaces.)

EPA did not provide a waiver of the HC limit in the final rule because: (1) the Agency believes, and SAB concurs, that a site-specific, health risk assessment approach to establishing HC limits (e.g., a waiver of the 20 ppmv limit) is not scientifically supportable; and (2) a technology-based waiver is not supportable because well-designed and operated hazardous waste combustion devices can readily meet a 20 ppmv HC limit.

Several commenters disagreed with EPA that both CO and HC should be monitored, stating that it is unnecessary to monitor CO if HC is monitored. The Agency continues to believe that it is reasonable to require both CO and HC monitoring when CO levels exceed 100 ppmv. When CO levels exceed the Tier I level, the facility is not operating at high combustion efficiency and the potential for high PIC emissions exists. The Agency believes that, since CO monitoring is a widely practiced approach for improving and monitoring combustion efficiency, and since CO emission levels may respond more quickly to process upsets than HC levels, the apparent redundancy in requiring both CO and HC monitoring is warranted to ensure protection of human health.

Another commenter added that HC monitoring could be supplemented by frequent testing for common PICs that respond poorly to HC monitors, such as carbon tetrachloride, formaldehyde, perchloroethylene, and chlorobenzene. At this time, the Agency believes that continuous HC monitoring combined with CO monitoring is adequate in most cases to detect when the facility is operating under combustion upset conditions (this is another reason, however, that monitoring both CO and HC is reasonable when CO levels exceed the level normally indicative of good combustion — 100 ppmv). We note that, as discussed in section II.D below, the final rule requires a hot HC monitoring system (i.e., unconditioned gas sample heated to a minimum of 150°C) which ensures minimum loss of organic compounds. Nonetheless, the Agency is currently developing sampling and analytical techniques to continuously monitor indicator organic compounds such as those suggested by the commenter.

We note that this approach should limit fuel-generated hydrocarbon concentrations to well below 20 ppmv because fuel-generated hydrocarbons from a well-designed and operated cement or light-weight aggregate kiln should not exceed 5 ppmv.

- e. Basis for Final Rule. EPA believes that the 20 ppmv HC limit in the final rule for the Tier II PIC controls is representative of an HC limit that distinguishes between good and poor combustion conditions. (When a facility operates under poor combustion conditions, PIC emissions can increase and may result in adverse health effects to exposed individuals.) This HC limit is within the range of values reported in the Agency's data base for hazardous waste incinerators, boilers, and industrial furnaces that burn hazardous waste, and the limit is also protective of human health based on risk assessments conducted for 30 incinerators. See 54 FR 43723. Under Tier II, HC must be monitored continuously, recorded on an hourly rolling average basis, reported as ppmv propane, and corrected to 7 percent oxygen on a dry basis. In addition, CO must be monitored continuously, corrected to 7 percent oxygen on a dry basis, recorded on an hourly rolling average basis, and may not exceed the limit established during the test burn (i.e., the average over all runs of the highest hourly rolling average for each run).
- 4. Special Requirements for Furnaces. The final rule provides several special requirements for industrial furnaces stemming from the fact that: (1) some industrial furnaces, notably cement kilns, are not able to meet the 20 ppmv HC limit because trace levels of organic matter in raw materials can emit substantial levels of hydrocarbons; and (2) the PIC controls may not be protective for furnaces (e.g., cement kilns and mineral wool cupolas) that feed hazardous waste at locations other than where normal fuels are fired. These special requirements are discussed below.
- a. Alternative HC Limit. EPA requested comment on whether alternative HC limits may be appropriate for certain industrial furnaces. See 54 FR 43724 (Oct. 26, 1989). A number of commenters<sup>28</sup> requested that EPA allow cement kilns, light-weight aggregate kilns, and lime kilns that cannot meet the 20 ppmv HC limit because of the hydrocarbons generated by trace levels of organic materials in the normal raw materials to establish a site-specific alternative HC limit that does not allow HC levels when burning hazardous waste to be significantly higher than when burning normal fuels, processing normal raw materials, and producing normal products in a system that is designed and operated to minimize hydrocarbon concentrations in stack gas. Nineteen commenters pointed out that

In addition to comments on the October 26, 1989 supplement to the proposed rule, see minutes of the EPA meetings with the Cement Kiln Recycling Coalition of April 17, 1990; May 23, 1990; June 4, 1990; June 20, 1990; July 19, 1990; and October 10, 1990. See also minutes of the EPA meeting with Southdown, Inc. on May 11, 1990, and the letter from the Cement Kiln Recycling Coalition to Bob Holloway, EPA, dated June 15, 1990.

baseline HC emission levels from cement kilns can be attributed to the naturally-occurring raw materials that are used in the production of cement. Use of shale as a raw material, for example, can result in HC emissions from kerogens in the shale. Use of fly ash as a source of iron and silica could result in increased CO emissions from partial oxidation of free carbon in the fly ash. Commenters claim that approximately 6 to 10 cement plants may not be able to comply with the HC limit of 20 ppmv even though they generate minimal HC from sources other than raw materials (e.g., hazardous waste fuels, other fuels, organic compounds in slurry water). The organic compounds in normal raw materials would not ordinarily be hazardous, so that their emissions (e.g., through volatilization) would not raise the types of concerns normally addressed by RCRA.<sup>29</sup>

The Agency believes that it will be possible in some situations to develop an approach on a case-by-case basis to effectively implement an alternative HC limit under the principle stated above. (If the 20 ppmv HC limit were health-based, the Agency would be more reluctant to develop an alternative to it. Given, however, that the limit is a measure of combustion efficiency, the Agency believes it reasonable to develop an alternative means for this class of furnaces to demonstrate combustion efficiency.) The Agency considered a number of approaches to establish an alternative HC level and determined in the time available that none appeared to be workable in all situations. The Agency is therefore adopting a more individualized approach in the present rule that allows permit writers to establish an alternative HC limit (i.e., a HC limit that exceeds 20 ppmv) in a facility's operating permit, and allows permit writers to grant an extension of time to comply with the HC limit during interim status, based on the following showings: (1) for cement kilns, the kiln is not equipped with a by-pass duct that meets the requirements of §266.104(f)(1); (2) the applicant demonstrates that the facility is designed and operated to minimize hydrocarbon emissions from fuels and raw materials; (3) the applicant develops an approach to effectively monitor over time changes in the operation of the facility that could reduce baseline HC levels -- for example, changes in raw materials, fuels, or operating conditions -- which could result in establishing a new baseline and corresponding adjustment of the HC limit; and (4) the applicant demonstrates that the hydrocarbon emissions are not likely to pose a significant health risk See §266.104(f)(2). We explain these provisions in more detail below, along with an explanation of which provisions apply during interim status and which are part of permit application and issuance.

We note, however, that nonhazardous organic constituents in feedstreams may be partially combusted to form hazardous products of incomplete combustion.

Interim Status Facilities. Today's rule requires facilities operating in interim status to comply with CO and, if required, a 20 ppmv HC limit within 18 months of the rule's date of promulgation. The rule provides for a case-by-case extension from these requirements (as well as the particulate, metals, and HCl/Cl<sub>2</sub> standards) "if compliance is not practicable for reasons beyond the control of the owner or operator." See §266.103(c)(7)(ii). The situation where a furnace may be unable to achieve the 20 ppmv HC limit because of organics present at baseline conditions (i.e., when the facility is designed and operated to minimize HC emissions from raw materials and fuels while producing normal products under normal operating conditions and when no hazardous waste is burned) may be eligible for the extension of time provided the following conditions are satisfied:

- 1. The applicant for the extension of time must have submitted a complete Part B permit application. The application must include the following information pertinent to the question of an alternative HC limit: (a) documentation that the system is designed and operated to minimize HC emissions from all sources when the baseline level is established and when hazardous waste is burned; (b) documentation of the baseline HC flue gas concentration when the facility is operated to minimize HC emissions and when feeding normal raw materials and normal fuels to produce normal products under normal operating conditions and when not burning hazardous waste; (c) a test protocol to confirm the baseline HC (and CO) level; (d) a trial burn protocol to demonstrate that, when hazardous waste is burned, HC (and CO) concentrations do not exceed the baseline level; and (e) a procedure to show if and when HC emissions from nonhazardous waste sources may decrease (in which case, the overall HC limit might be adjusted downward after a new baseline is established). See §270.22(b). (The substantive basis for these requirements is explained in more detail below.)
- 2. During interim status, the applicant must not only conduct emissions testing when burning hazardous waste to certify compliance with all remaining emissions controls dioxins and furans, PM, metals, and HCl/Cl2 -- but also establish and comply with interim limits on CO and HC presented in the Part B permit application as levels the applicant has determined by testing (without burning hazardous waste) are baseline levels. We note that the Director may not have time during the review of the extension request (and a preliminary review of the Part B application) to confirm the adequacy of the interim CO and HC limits proposed by the applicant. Moreover, to do so would require the types of oversight of test protocols, emissions testing, and review of data that will be applied under the permit process. Thus, the interim limits are subject to revision based on (confirmation) testing in support of the operating permit. Nonetheless, EPA believes that establishing interim CO and HC limits and requiring the owner/operator to comply with them until a permit is issued (or denied) is reasonable and provides a measure of protection of human health and the environment.

It should be noted that the Agency does not believe that it is possible to establish an alternative HC limit during interim status. This is because the level of interaction between an applicant and permit writer over evaluation of the various protocols to establish a HC baseline and determine when it should be reduced, plus conducting

test burns to confirm the HC baseline and that HC levels do not increase when hazardous waste is burned, plus conducting a health-risk assessment for organic emissions when hazardous waste is burned are beyond the scope of interim status. Consequently, the rule is structured so that the alternative HC limit (if warranted) would be established as part of the permit, and the interim status certification of compliance deadline can be extended, if the Director finds this is warranted, while the permit is being processed. The Director may also may make the extension of time conditional on the time estimated to process the permit application or other factors, and can be conditioned on operating conditions than ensure the facility will operate in a manner that protects human health and the environment. Any such condition would be embodied in an interim status extension determination that is enforceable as a requirement of subtitle C (much as conditions in a closure plan are enforceable), and would be documented in an administrative record for the determination.

3. Cement kilns with a by-pass duct are ineligible for an extension. The rule precludes cement kilns operating with a by-pass duct from eligibility for the extension of the certification of compliance date for compliance with the CO and HC limit, as well as for obtaining an alternative HC limit in a permit.

Fully Permitted Facilities. The Director may establish an alternative HC limit in the facility's operating permit provided that the applicant meets the following requirements. Information and data documenting compliance with these requirements must be included in the Part B permit application. See §270.22(b). First, the applicant must document in the permit application that facility is designed and operated to minimize HC emissions from all sources, including raw materials and fuels. Examples of situations where the system is not designed and operated to minimize HC (and CO) levels during baseline testing are when:

(1) coal is mixed with raw material which is fed into a cement kiln preheater such that the coal can contribute to HC emissions; (2) cement kiln slurry water contains enough organic compounds to significantly contribute to HC emissions; (3) waste fuels such as tires are burned in a manner that could contribute to HC emissions; (4) the furnace is not operated and designed to minimize emissions of hydrocarbons emitted from raw material (in general, the more quickly the raw material is exposed to elevated temperatures, the lower the hydrocarbon emissions); and (5) normal fuels are not burned under good combustion conditions.

Second, the applicant must propose in the permit application baseline flue gas CO and HC levels. These proposed baseline levels also serve as interim values under which the facility must operate under a conditional time extension for certification of compliance with the HC standard until permit issuance (or denial). The proposed baseline levels must be supported by emissions testing under baseline conditions (i.e., when the facility is designed and operated to minimize HC emissions from raw materials and fuels while producing normal products under normal operating conditions and when no hazardous

waste is burned). Baseline levels must be determined from test data as the average over all valid runs of the highest hourly rolling average value for each run. This is the same approach specified by the rule to determine limits on other operating parameters (e.g., maximum feed rate limits, maximum temperatures, etc). EPA believes that this approach is workable for cement kilns<sup>30</sup> given that commenters have asserted that when hazardous waste is burned, hydrocarbon levels do not increase and often decrease. As discussed in section II.E of Part Three of the preamble, HC levels from a cement kiln with HC levels of 66 to 70 ppmv when burning coal decreased to 38 to 63 ppmv when burning hazardous waste fuel. If the facility cannot install continuous monitors for HC (and CO and oxygen) in time to conduct these baseline tests prior to submittal of the permit application (which must be sufficiently prior to 18 months after promulgation of the rule to give the Director time to consider whether to grant the time extension), the facility may use portable monitors. We note that the HC monitoring system must be a hot, unconditioned system. In addition, we note that different baseline values may be necessary for different modes of operation if the baseline HC (or CO) level changes significantly under those modes of operation. Examples are when the raw material mix is changed to make a different cement product or when different fuels are burned.

Third, the applicant must develop emissions testing protocols to: (1) confirm the baseline HC and CO levels proposed in the permit application (and under which the facility must operate in interim status upon receipt of an extension of time to comply with the HC limit and until an operating permit is issued (or denied)); and (2) to demonstrate that, when hazardous waste is burned, HC and CO levels do not exceed baseline levels (and emissions of other pollutants do not exceed allowable levels). If a baseline HC or CO level is to be established for more than one mode of operation, a baseline confirmation test (comprised of at least three valid runs) must be run for each mode.

Fourth, the applicant must develop an approach to effectively monitor over time changes in the operation of the facility that could significantly reduce baseline HC or CO levels. If baseline levels are significantly reduced, then the alternative HC and CO limits that apply when burning hazardous waste must also be reduced. Such changes could include: (1) changes in the concentration of organic matter in raw materials; (2) changes in the concentration of organic matter in the raw material mix due to changes in the mixture of

Although any industrial furnace that cannot meet the 20 ppmv HC limit because of organic matter in raw material is eligible to apply for an alternative HC limit, only one commenter expressed concern that industrial furnaces other than cement kilns may not be able to meet the 20 ppmv HC limit.

raw materials needed to produce different types of product; (3) changes in fuels; and (4) changes in the concentration of organic compounds in slurry water used for a wet cement kiln. The approach must be workable and enforceable.

EPA is requiring this condition in order to avoid establishing a high baseline which is then reduced without also lowering the HC limit, potentially allowing the hazardous waste to be burned under poor combustion conditions creating high, but undetected, HC levels (i.e., hazardous waste could be burned under poor combustion conditions and could be emitting high HC levels even though the HC limit was not exceeded). (The Agency notes that the problem of establishing a HC baseline and for determining when the baseline might change for this type of industrial furnace is more difficult than determining when the raw material baseline changes in documenting when co-combustion of hazardous waste with raw materials in a Bevill device might affect the composition of residues. See section XIII of Part Three of the preamble. This is because, in the case of the HC baseline, not only must the raw materials' and fuels' composition be monitored, but the units design and operating conditions as well to determine whether the baseline has changed. Thus, the rule provides for more interaction in establishing baseline conditions and determining when they change for assessing alternative HC limits for cement kilns than it does when making determinations as to whether co-combustion of hazardous waste can remove residues from eligibility for exclusion under the Bevill amendment.)

Finally, EPA is concerned that hazardous waste burning may affect the type and concentration of organic compounds emitted from an industrial furnace that has elevated HC concentrations attributable to raw materials. For example, the chlorine in the hazardous waste may result in higher concentrations of chlorinated organic compounds. Therefore, the rule requires the owner or operator, as part of the permitting process, to use state-of-the-art emissions testing procedures and risk assessment to demonstrate that organic emissions are not likely to pose unacceptable health risk. The owner or operator must conduct emissions testing during the trial burn to identify and quantify the organic compounds listed in Appendix VIII, Part 261, that may be emitted using test procedures specified by the Director on a case-by-case basis. As noted above, although EPA does not believe such risk-based approaches to be adequate as the basis for a national risk-based PIC standard, we think the approach is part of the best means of assuring that cement kilns combust hazardous waste fuels properly in those instances where HC levels are greater than 20 ppmv as a result of organics in normal raw material feed.

Two sampling and analysis approaches that the Director may use are discussed below. One protocol involves the following steps to identify and quantity concentrations of organic compounds in stack emissions:

- 1. Sample volatile organic compounds using the VOST train of Method 0030 as prescribed in SW-846 Analytical work is conducted using GC/MS according to Method 5040 in SW-846.
- 2. Sample semi-volatile organic compounds using the sampling train prescribed in Method 0010 in SW-846. Analytical work is conducted using GC/MS according to Method 8270 in SW-846.
- 3. Sample aldehydes and ketones using an impinger train with 2-4 di-nitro-phenyl hydrazine (2-4 DNPH) in the impinger solution as prescribed in Method 0011 in the Methods Manual, and analysis of impinger solution by high performance liquid chromatography (HPLC) as specified in "Analysis for Aldehydes and Ketones by High Performance Liquid Chromatography" in the Methods Manual.

Another protocol is a screening approach that has been described in the literature<sup>31</sup> that uses the following protocols as specified in SW-846:

- 1. Soxhlet extraction sample preparation;
- 2. Gas chromatography (GC) coupled with flame ionization detector (FID) or mass spectrography (MS) screening;
- 3. Total chromatographic organics (TCO) and gravimetric (GRAV) procedures; and
- 4. High performance liquid chromatography-ultraviolet/MS (HPLC-UV/MS) screening and compound identification.

To select an appropriate protocol, the Director will consider the state-of-the-art of sampling and analytical techniques and the expected nature of organic emissions considering emissions data or other information.

We note that, under this PIC risk assessment, emission rates must also be determined for the 2,3,7,8-chlorinated tetra-octa congeners of chlorinated dibenzo-p-dioxins and dibenzofurans (CDDs/CDFs) using Method 23, "Determination of Polychorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans (PCDFs) from Stationary Sources" in Methods Manual for Compliance with the BIF Regulations

Johnson, Larry, et. al., "Screening Approach for Principal Organic Hazardous Constituents and Products of Incomplete Combustion", JAPCA Journal, Volume 39, No. 5, May 1989.

(Methods Manual) (incorporated by reference in §261.11). The risks from these congeners must be estimated using the 2,3,7,8-TCDD toxicity equivalence factor prescribed in "Procedures for Estimating the Toxicity Equivalence of Chlorinated Dibenzo-p-Dioxin and Dibenzofuran Congeners" in (Methods Manual.

The owner or operator must then conduct dispersion modeling to predict the maximum annual average ground level concentration of each such organic compound. Onsite ground level concentrations must be considered if a person resides on-site; otherwise, only off-site concentrations may be considered. Dispersion modeling must be conducted in conformance with EPA's <u>Guideline on Air Quality Models</u>, EPA's "Hazardous Waste Combustion Air Quality Screening Procedure" provided in <u>Methods Manual</u>, or EPA's <u>Screening Procedures for Estimating Air Quality Impact of Stationary Sources</u>. All three documents are incorporated by reference in §260.11.

Stack heights exceeding good engineering practice (GEP, as defined in 40 CFR 51.100(ii)) may not be used to predict ground level concentrations. See section V.B.1.c of Part Three of this preamble.

If the owner or operator applies for an alternative hydrocarbon limit for more than one industrial furnace such that emissions from the furnaces are from more than one stack, emissions testing must be conducted on all such stacks and dispersion modeling must consider emissions from all such stacks.

To demonstrate that the noncarcinogenic organic compounds listed in Appendix IV of the rule do not pose an unacceptable health risk, the predicted ground level concentrations cannot exceed the levels established in that Appendix.

To demonstrate that the carcinogenic organic compounds listed in Appendix V of the rule do not pose an unacceptable health risk, the sum of the ratios of the predicted ground level concentrations to the levels established in the Appendix cannot exceed 1.0. This is because the acceptable ambient levels established in Appendix V are based on a 10<sup>-5</sup> risk level. To ensure that the summed risk from all carcinogenic compounds does not exceed 10<sup>-5</sup> (i.e., 1 in 100,000) the sum of the ratios described above must be used. (We note that the 2,3,7,8-TCDD toxicity equivalency factor is to be used to estimate the risk from 2,3,7,8-chlorinated CDDs/CDFs, and the risk from these congeners must be added to the risk from other PICs to ensure that the summed risk does not exceed 1 in 100,000.)

To demonstrate that other compounds for which the Agency does not have adequate health effects data to establish an acceptable ambient level are not likely to pose a health risk, the predicted ambient level cannot exceed 0.09 ug/m<sup>3</sup>. This is the 5th percentile lowest reference air concentration for the compounds listed in Appendix IV of the rule.

b. Feeding Waste at Locations other than the Hot End. If hazardous waste is fed into an industrial furnace at locations other than the "hot" end where the product is normally discharged and where fuels are normally fired, the rule requires the owner/operator to monitor HC irrespective of whether CO levels do not exceed the Tier I limit of 100 ppmv and to comply with special restrictions during interim status. These provisions are discussed below.

Mandatory HC Monitoring<sup>32</sup>. Except as indicated below, facilities that fire hazardous waste into an industrial furnace at locations other than the "hot" end where the product is normally discharged and where fuels are normally fired must comply with the HC limit even if CO levels do not exceed the Tier I limit of 100 ppmv. See §266.105(d). This is because the Agency is concerned that the hazardous waste could conceivably be fired at a location in a manner such that nonmetal compounds in the waste may be merely evaporated or thermally cracked to form pyrolysis by-products rather than completely combusted. If so, little CO may be generated by the process and, thus, monitoring CO alone would not ensure that HC emissions were minimized.

However, if hazardous waste is burned (or processed) solely as an ingredient, HC monitoring is not automatically required because emissions of nonmetal compounds are not of concern. This is because the metals emissions controls will ensure that metals emissions do not pose a hazard. (The rule establishes the restrictions discussed below because we are concerned that the interim status controls on <u>organic</u> emissions may not be protective when hazardous waste is fed at locations other than the "hot" end of a furnace.) See discussion in section VII.H of Part Three of this preamble for when a waste is considered to be burned solely as an ingredient<sup>33</sup>.

Continuous HC monitoring is required for a furnace if hazardous waste is fired at any location other than the "hot", product discharge end where fuels are normally fired irrespective of the CO level in stack emissions (i.e., irrespective if CO levels are lower than the Tier I limit of 100 ppmv) and irrespective of whether furnace off-gas is passed through another combustion chamber.

Regulated entities have indicated that there is substantial confusion over the terms "use as an ingredient" and "material recovery". Under the RCRA hazardous waste

Interim Status Restrictions. In addition to requiring HC monitoring when hazardous waste is fed into a furnace at locations other than the "hot" end where the product is discharged and where fuels are normally fired, today's rule applies other restrictions to hazardous waste burning during interim status. See §266.104(a)(5). The hazardous waste may not be fed at any location where combustion gas temperatures are less than 1800°F, and the owner or operator must demonstrate that adequate oxygen is present to combust the waste. In addition, for cement kilns, the hazardous waste must be fed into the kiln itself. These requirements are provided to ensure adequate destruction of the waste given that the DRE standard (which requires a demonstration by trial burn that organic constituents in the waste are destroyed) is not applicable during interim status. Like the requirement for mandatory HC monitoring, however, these restrictions do not apply if the hazardous waste is burned (processed) solely as an ingredient. For further discussion, see section VII.H of Part Three of this preamble.

- 5. Special Considerations for Cement Kilns.
- a. Monitoring in the By-Pass Duct of a Cement Kilns. The final rule provides that cement kilns with by-pass ducts may monitor CO and, if required, HC concentrations in the by-pass duct. Most precalciner and some preheater kilns are equipped with by-pass ducts where a portion (e.g., 5-30%) of the kiln off-gas is diverted to a separate air pollution control system (APCS) and, sometimes, a separate stack. A portion of the kiln gases are so diverted to avoid a build-up of metal salts that can adversely affect the calcination process. Dust collected from the by-pass APCS is usually disposed of while dust collected from the main APCS is usually recycled back into the kiln to make the clinker product.

Several comments were received regarding sampling at cement kilns. Five commenters suggested that HC (and CO) measurements should be allowed in the bypass duct rather than in the main stack because: (1) the by-pass gas is representative of the kiln off-gas; and (2) this approach would preclude the problem of nonfuel HC emissions from the raw material exceeding the 20 ppmv limit. The raw material would be heated and partially calcined in the precalciner or preheater and HC from that process would be emitted

regulatory program, EPA considers a hazardous waste to be burned or processed as an ingredient if it is used to produce a product. EPA considers a hazardous waste to be burned or processed for material recovery if one or more constituents of the waste is recovered as a product.

from the main stack. The by-pass duct draws the kiln off-gas prior to the precalciner or preheater and, so, would not be affected by that process.

Another commenter specifically supported monitoring CO (and HC, if required) only in the bypass duct provided that hazardous waste is fed only to the kiln and not to the preheater or precalciner.

The Agency conducted testing<sup>34</sup> at a cement kiln to gather information relevant to the issue of HC monitoring in the bypass duct for preheater and precalciner cement kilns. The data showed that the gases in the bypass duct are representative of the combustion of waste in the kiln.

Based on this test data and public comment, the final rule allows CO and, where required, HC monitoring in the by-pass duct of a cement kiln provided that: (1) hazardous waste is fired only into the kiln (i.e., not at any location downstream from the kiln exit relative to the direction of gas flow); and (2) the by-pass duct diverts a minimum of 10% of kiln off-gas. See §266.104(f)(1). The 10% diversion requirement is based on engineering judgment that, at this level of kiln-gas diversion, the by-pass gas will be representative of the kiln off-gas. Industry representatives indicate<sup>35</sup> that the by-pass duct capacity of most facilities actively involved in burning hazardous waste exceeds the 10% limit.

b. Use of Hazardous Waste as Slurry Water for Wet Cement Kilns. Some kiln operators have inquired as to what regulatory standards apply, if any, if hazardous wastes are used as slurry water. The Agency does not regard the practice as an excluded form of recycling. The Agency has long been skeptical of claims that hazardous wastes are "recycled" when they substitute for very commonly available and economically marginal types of raw materials. In particular, the Agency has been skeptical that liquid hazardous wastes serve as a substitute for water. Cf. 48 FR at 14489 (April 4, 1983). In the case of hazardous waste used as slurry water, the hazardous constituents in the waste are ordinarily unnecessary to the claimed recycling activity and are being gotten rid of through the slurrying process. Given the possibility of hazardous levels of air emission is high, the practice certainly can be part of the waste disposal problem. Consequently, the Agency

U.S.EPA, "Emissions Testing of a Precalciner Cement Kiln at Louisville, Nebraska", November 1990.

Letter dated August 16, 1990, from Dr. Michael von Seebach, Southdown, Inc., to Dwight Hlustick, EPA.

regards such practice as a form of waste management subject to regulation under today's rule.

EPA considered prohibiting the use of hazardous waste as slurry water for wet cement kilns because of concern that toxic organic constituents in the waste could be volatilized and emitted without complete combustion. The final rule does not prohibit using (or mixing) hazardous waste with slurry water because we believe that the controls provided by the rule both during interim status and under a RCRA operating permit adequately addresses the hazard that the practice may pose.

If hazardous waste is fed into any industrial furnace during interim status at a location other than the hot, product discharge end, combustion gas temperatures must exceed 1800°F at the point of introduction, and the owner or operator must document that adequate oxygen is present to combust organic constituents in the waste. See discussion above. EPA believes that these restrictions will, as a practical matter, preclude use of hazardous waste in slurry water during interim status.

Although these restrictions on hazardous waste burned at locations other than the hot end of an industrial furnace do not apply under a RCRA operating permit, the permit proceedings will ensure that organic constituents in a hazardous waste that is fed into the kiln in slurry water (or in the slurry itself) will be destroyed. The Director will require that, toxic nonmetal constituents in the waste are destroyed to a 99.99% destruction and removal efficiency, and that adequate oxygen is present to completely destroy the organic compounds.

#### C. Automatic Waste Feed Cutoff Requirements.

Today's rule requires that boilers and industrial furnaces combusting hazardous waste be equipped with automatic waste feed cutoff systems to limit emissions of hazardous compounds during combustion "upset" situations and to ensure stable combustion conditions. The automatic waste feed cutoff system must be connected to the CO and HC monitoring system, such that an exceedance of a CO or HC limit would trigger a cutoff of the waste feed. Additionally, the automatic waste feed cutoff system must engage when other key operating conditions deviate from specified unit operating limits, which are determined during compliance testing or which are based on manufacturer specifications. See §§266.102(e)(7)(ii) and 266.103(h).

Some commenters disagreed with the proposed automatic waste feed cutoff requirements. One commenter argued against any waste feed cutoffs for light-weight aggregate kilns. Six commenters expressed concern that waste feed cutoffs would increase the instability of the combustion conditions and would possibly increase air emissions. Three commenters requested a controlled waste feed reduction over several minutes rather than an automatic waste feed shutoff. Three commenters suggested different levels of CO emissions be set for waste feed cutoffs.

The Agency acknowledges that there can be performance and other problems associated with automatic waste feed cutoffs, and recognizes that they may be undesirable for some applications. For example, when the facility operates without the use of hazardous waste fuel, use of fossil fuel is increased, and the opportunity is lost for safe disposal of hazardous waste. Further, HC emissions may actually increase if the automatic waste feed cutoff is triggered frequently even though combustion chamber temperatures must be maintained while hazardous waste or residues remain in the combustion chamber. However, the Agency continues to believe that automatic waste feed cutoff systems are necessary to avoid adverse effect on human health and the environment that could result if hazardous waste is fired into the device when it is operating under combustion upset conditions.

To address the concerns raised by commenters, EPA recommends installing prealarm systems that alert an owner/operator of potential problems and provide time either for corrective measures to be taken or for a staged cutoff of the hazardous waste feed. Thus, the use of pre-alarms should minimize waste feed cutoffs. In addition, we have included in the rule some additional requirements related to waste feed cutoffs and restarts, as discussed below.

One commenter stated that cutoffs are inappropriate for combustion devices where the waste is destroyed immediately upon injection into the combustion chamber (e.g., devices that burn liquid wastes), or if the combustion conditions supported by the waste fuel continue to destroy residual waste after waste feed cutoff. The Agency continues to believe that the best method for returning a combustion system to good operating conditions, thereby minimizing unacceptable emissions, is to stop the input of hazardous waste. Further, the burden associated with automatic cutoffs should not be substantial because frequent automatic waste feed cutoffs should not occur given that the parameters tied into the automatic cutoff system may be monitored on a hourly rolling average basis

(which allows high values to be off-set by low values) and that the Agency recommends the use of pre-alarms to warn the operator of a pending cutoff (which may give the operator time to take corrective measures to avoid an automatic cutoff).

In the event of a waste feed cutoff, monitoring for CO and HC (and other operating parameters for which limits in the permit are based on a rolling average basis) must continue, and the waste feed cannot be restarted until CO and HC levels (and levels of the other parameters) come within allowable limits. See \$266.102(e)(7)(ii). (For permit operating conditions not established on a rolling average basis, the Director will specify, on a case-by-case basis, an adequate period of time during which the parameters must remain within permit limits to demonstrate steady-state operation prior to restarting the hazardous waste feed.) In addition, consistent with the April 27, 1990 incinerator amendments proposal, the provision of the final boiler and industrial furnace rule requiring compliance with the permit operating conditions states that compliance must be maintained at any time there is waste in the unit. See \$266.102(e)(1). This language clarifies that activation of the automatic waste feed cutoff does not relieve the facility of its obligation to comply with the permit conditions if there is waste remaining in the unit (such as in a rotary kiln). Thus, for example, the air pollution control system must continue to be operated within the applicable permit conditions.

Furthermore, after a cutoff, the temperature in the combustion chamber must be maintained at levels demonstrated during the compliance test for as long as the hazardous waste or residue remains in the combustion chamber. The Agency believes this temperature requirement will help ensure that hydrocarbon emissions will be minimized after a cutoff.

To comply with this requirement, the operating permit must specify the minimum combustion chamber temperature after a waste feed cutoff while waste remains in the combustion chamber. An uninterruptable burner using auxiliary fuel (i.e., nonhazardous waste fuel) of adequate capacity may be needed to maintain the temperature in the combustion chamber(s) and to allow destruction of the waste materials and associated combustion gases left in the system after the waste feed is automatically cut off. The safe startup of the burners using auxiliary fuel requires approved burner safety management systems for prepurge, pilot lights, and induced draft fan starts. If these safety requirements preclude immediate startup of auxiliary fuel burners and such startup is needed to maintain temperatures (i.e., if the combustion chamber temperatures drop precipitously after waste

feed cutoff), the auxiliary fuel may have to be burned continuously on "low fire" during nonupset conditions.

Furthermore, §266.102(e)(7)(ii)(B) requires that the combustion gases must continue to be routed through the air pollution control system as long as waste remains in the unit. One effect of this clarifying requirement, in combination with the requirement to maintain compliance with permit conditions as long as there is waste in the unit, is that opening of any type of air pollution control system bypass stack while there is waste in the boiler or furnace would be a violation of the permit (unless the facility demonstrates compliance with the performance standards during the trial burn, with the vent stack open).

Although we believe that such emergency bypass stacks are not prevalent on boilers and industrial furnaces, our discussion of this topic in the preamble to the incinerator amendments at 55 FR 17890 (April 27, 1990) would also apply to any boiler or industrial furnace with such a bypass or vent stack. We received a number of comments from the incinerator industry expressing concern that use of a bypass stack for safety purposes would be considered a violation. We agree that there can be mitigating circumstances to discredit their use as a safety device. However, the Agency continues to believe that the facility can and should implement measures to minimize situations where use of the emergency vent stack is necessary.

One commenter stated that the use of hazardous waste should be prohibited during startup or shutdown periods for a cement kiln until normal operating temperatures are achieved. The final rule does not restrict hazardous waste burning during kiln startup or shutdown provided that the compliance (or trial burn) covers those periods of operations. In other words, hazardous waste may be burned during startup and shutdown if the facility demonstrates conformance with the standards during those operations.

Another commenter argued that accurate measurement of combustion chamber temperature for some combustion devices will be difficult. Because of this difficulty, the final rule does not require that this temperature be directly measured in the combustion chamber if an owner/operator can demonstrate to permitting officials that the combustion chamber temperature correlates with a more easily measured downstream gas temperature.

One commenter agreed with EPA's revised proposal not to limit the number of automatic waste feed cutoffs, but disagreed with EPA's requirement that combustion chamber temperatures must be maintained at the levels that occurred during the trial burn

for the duration of time that the waste remains in the combustion chamber. This commenter believed that electric utility boilers and other burning devices will have difficulty in accurately measuring combustion chamber temperatures. For this reason, the commenter suggested that waste feed cutoffs alone be used to control HC emissions rather than also requiring that combustion chamber temperatures be maintained. EPA believes that the flexibility that the final rule allows for monitoring combustion chamber temperature and in setting the frequency of waste feed cutoffs as discussed above should address this commenter's concerns.

Another commenter supported the proposed 10 times per month limit on the number of automatic waste feed cutoffs and the proposed requirement that any facility exceeding that frequency would be required to cease burning hazardous waste, to notify the Director, and not to resume burning hazardous waste until reauthorized by the Director. Another commenter supported monthly cutoff limits because they would provide an incentive for the facility to take corrective measures to preclude frequent cutoffs. Some commenters stated that this requirement is overly restrictive.

After careful consideration, EPA has decided to modify this requirement for the following reasons: (1) the Agency does not have data indicating a specific frequency of cutoffs which would be unacceptable at all boilers and furnaces given that the combustion chamber temperature and other conditions are maintained as described above; (2) the Agency believes that operating costs associated with cutoffs will provide sufficient incentive to encourage owners/operators to minimize automatic waste feed cutoff incidents; and (3) the recommended use of pre-alarm systems will reduce the number of waste feed cutoffs. However, the final rule allows the Director to use his discretion to determine whether a limit on the frequency of cutoffs is warranted at a specific facility.

Waste Feed Restarts. Today's rule provides that when the automatic waste feed cutoff is triggered by a CO limit or when applicable, an HC exceedance, the waste feed can be restarted only when the hourly rolling average CO/HC levels meet the permitted limits (e.g., 100 ppmv for CO under Tier I).

The Agency proposed two alternative approaches for restarting the waste feed when a cutoff is triggered by a CO exceedance: (1) restart the waste feed after an arbitrary 10-minute time period to enable the operator to stabilize combustion conditions; or (2) restart the waste feed after the instantaneous CO level meets the hourly rolling average limit. Eight commenters supported restarting the waste feed after the instantaneous CO level meets the

permit limit. Five commenters suggested that waste feed can be restarted once the instantaneous CO level meets the hourly rolling average limit. The Agency considered the comments, but continues to believe that allowing a waste feed restart after the hourly rolling average equals or falls below the permitted limit is preferable. After the waste feed is cutoff, the facility will be burning nonhazardous waste (typically fossil fuel), which should result in CO and HC levels well below the allowable limits. Therefore, the hourly rolling average should fall below the permitted limit within a relatively brief period of time. Allowing the waste feed to be restarted when the instantaneous CO level has dropped to the permitted level may not be desirable, because restarting the waste feed immediately may trigger another cutoff due to a CO spike when the waste feed is restarted.

Three commenters supported the proposed approach to require the HC hourly rolling average to be met before restarting the waste feed cutoff because of a HC exceedance. Three commenters opposed this approach. Instead, these commenters suggested a 10-minute waiting period be used. EPA considered these comments but continues to believe that meeting the hourly rolling average is a conservative approach and is appropriate after a HC exceedance, because the HC is a better surrogate for toxic organic emissions than CO.

## D. CEM Requirements for PIC Controls.

The final rule promulgates the proposed performance specifications for continuously monitoring CO, HC, and oxygen. See Methods Manual for Compliance with the BIF Regulations, incorporated by reference in today's rule in §260.11. The performance specifications for HC monitoring, however, include specifications for both hot and cold monitoring. Although hot monitoring is generally required by the final rule, cold monitoring may be used for interim status facilities if they certify compliance with the emissions standards within 18 months of promulgation of the rule. Even if cold monitoring is used to certify initial compliance, however, hot monitoring is required for these facilities when they recertify compliance and when they are issued a RCRA operating permit.

One commenter stated that an HC monitoring system is readily available for continuous emissions monitoring (CEM), while five commenters maintained that HC analyzers have serious operational problems. Several commenters requested that alternate HC CEM methods be allowed, specifically monitors with non-dispersive infra-red (NDIR) detectors rather than the required flame ionization detector (FID). One commenter noted

that EPA has not validated the FID method for HC analysis nor has it provided any critical discussion of the current methods of HC analysis.

The Agency considered the use of NDIR detectors for HC monitoring but believes that NDIR systems have limitations compared to FID systems. EPA believes that FID systems are more sensitive than NDIR systems and that an equivalent response is not found with NDIR detectors. The final rule requires the use of FID detectors for HC monitoring.

Four commenters recommended monitoring nonmethane hydrocarbons (NMOC) as opposed to "total" HC because methane, which is predominantly emitted from fuel sources, has a high FID response factor. Furthermore, these commenters would like EPA to require testing for specific PICs that respond poorly to HC monitors during test burns. One commenter stated that HC monitors can be varied easily to detect NMOC. EPA does not agree with either suggestion. The Agency is requiring HC monitoring to indicate whether the device is operating under good combustion conditions. We acknowledge that the largest fraction of organic compounds that the HC monitoring system required by the final rule will detect for facilities operating under good combustion conditions will be compounds that are relatively nonhazardous (e.g., methane). In addition, some hazardous compounds, particularly highly chlorinated compounds) will be under-reported. Thus, although the promulgated approach would not be adequate for the purpose of assessing the risk that HC may pose from a given facility, the approach is adequate for its intended purpose -- a measure of whether the facility continues to operate within good combustion conditions. This is because EPA's emissions testing has shown that when combustion conditions deteriorate, the compounds that are readily detected by the promulgated HC monitoring system increase correspondingly.

In addition, if a NMOC system were used, the 20 ppmv HC limit would have to be lowered to account for the methane fraction that would no longer be counted. Commenters did not provide support for so adjusting the proposed HC limit. Further, the Agency is concerned that NMOC detectors may not be able to provide continuous data due to the time required for methane separation. The Agency has also found that HC CEMs are more durable than NMOC CEMs, and thus less prone to reliability problems. As a result, the Agency has concluded that HC CEMs are more likely to provide a continuous indication of combustion conditions than is possible with an NMOC monitor.

Hot Versus Cold HC Monitoring Systems. Except as indicated below, the final rule requires the use of a hot or unconditioned HC monitoring system that must be

maintained at a temperature of at least 150°C until the sample gas exits the detector. See performance specifications in Methods Manual for Compliance with the BIF Regulations (incorporated by reference, see §260.11). Given, however, that the technology has just recently been demonstrated<sup>36</sup> to be continuously operational on hazardous waste combustion devices, the final rule allows the use of a conditioned gas monitoring system during the initial phase of interim status operations. Facilities in interim status that certify compliance with the emission standards for metals, HCl, Cl<sub>2</sub>, particulate matter, CO and HC within 18 months of promulgation of the final rule may obtain an automatic waiver to use a conditioned gas system. Facilities that elect to obtain the automatic 12-month extension (or a case-by-case extension) of the 18-month certification deadline, however, are not eligible for the waiver because the additional time provided by the extension will also provide time to install an unconditioned HC monitoring system. These facilities must demonstrate compliance with the HC limit using an unconditioned gas monitoring system. Further, facilities that certify initial compliance using a conditioned gas (cold) system must use an unconditioned gas (hot) system when they recertify compliance within three years of certifying initial compliance.

EPA is requiring the use of a hot monitoring system because it represents best demonstrated technology given that a larger fraction of HC emissions can be detected with a hot system. As discussed at proposal, a hot HC monitoring system can detect a substantially larger fraction of hydrocarbon emissions than a cold system. This is because the cold system uses a gas conditioning system that removes semi- and nonvolatile hydrocarbons and a substantial fraction of water-soluble volatile hydrocarbons.

EPA received numerous comments regarding gas conditioning (heated versus unheated) for HC monitoring. Eight commenters are in favor of gas conditioning. The purpose of gas conditioning is to remove moisture from the combustion gases that can degrade instruments or plug sample lines. Sample conditioning, however, can also remove some of the water soluble hydrocarbons and the semi and nonvolatile hydrocarbons in the flue gas such that methane and other nonhazardous volatile hydrocarbons are frequently the dominant constituents measured by the detector. Some commenters were concerned that fewer PICs would be detected by a conditioned (i.e., cooled) monitoring system.

Entropy Environmental Inc., "Evaluation of Heated THC Monitoring Systems for Hazardous Waste Incinerator Emission Measurement", Draft Final Report, October 1990; and Shamat, Nadim, et al, "Total Hydrocarbon Analyzer Study", Paper presented at the 63rd Water Pollution Control Federation Conference in Washington, D.C., October 8, 1990.

However, one commenter stated that even though the constituents contributing most of the hypothetical risk are relatively nonvolatile they are relatively nondetectable through an unconditioned (heated) monitoring system because of their halogen content.

As discussed at proposal, the Agency is using HC monitoring to implement the technology-based HC limit of 20 ppmv as an indicator of good combustion conditions. The HC monitor is not used in an attempt to quantify organic emissions for risk assessment purposes. Emissions testing has shown that during combustion upset condition, both the hot and cold HC monitoring systems detect an increase in HC levels because under upset conditions there is a substantial increase in hydrocarbon compounds that are readily detected by either monitoring system.<sup>37</sup>

One commenter suggested that, rather than specifying a range of 40-64°F for operation on the conditioner as proposed, a specific conditioning temperature (32°F) should be required to precisely define the conditioned sampling procedure. We agree that a minimum temperature should be specified rather than the range. The final rule allows a conditioned monitoring system during the initial phase of interim status, and requires that the sample gas temperature must be maintained at a minimum of 40°F at all times prior to discharge from the detector. EPA selected a minimum temperature of 40°F from the range of 40 to 64°F to ensure that moisture was effectively removed from the gas sample to preclude plugging and fouling problems with the monitoring system.

Three commenters suggested that the HC limit of 20 ppmv be re-examined because gas conditioning temperatures or other changes in the measurement method may influence the amount of HC measured. Given that the 20 ppmv limit is based primarily on test burn data using heated (i.e., unconditioned) monitoring systems, the Agency considered lowering the 20 ppmv limit when a cold (i.e., conditioned) monitoring system is used. (Limited field test data indicate that a heated system would detect from 30% to 400% more of the mass of organic compounds than a conditioned system.) We believe, however, that the 20 ppmv HC limit is still appropriate when a conditioned system is used because: (1) the data correlating heated vs conditioned systems are very limited; (2) the data on HC emissions are limited (and there apparently is confusion in some cases as to whether the

EPA is requiring the use of a hot, unconditioned HC monitoring system (except under certain circumstances during the initial phase of interim status) because hot systems are, nonetheless, more conservative in that they detect a larger fraction of organic compounds in emissions. Further, hot systems represent best demonstrated technology for monitoring HC levels.

data were taken with a conditioned or unconditioned monitoring system); and (3) the Agency's risk methodology is not sophisticated enough to demonstrate that a HC limit of 5 or 10 ppmv using a conditioned system rather than an unconditioned system is needed to protect human health and the environment. The SAB<sup>38</sup> also concurs with this view. (More detailed responses to comments on this issue are found in a separate background document.)

# E. Control of Dioxin and Furan Emissions.

For facilities that may have the potential for significant emissions of chlorinated dibenzodioxins and dibenzofurans (CDD/CDF), the final rule requires emissions testing for both interim status and new facilities to determine emissions rates of all tetra-octa congeners, calculation of a toxicity equivalency factor, and dispersion modeling to demonstrate that the predicted maximum annual average ground level concentration (i.e., the hypothetical maximum exposed individual) does not exceed levels that would result in an increased lifetime cancer risk of more than 1 in 100,000.<sup>39</sup> The Agency considers a facility to have the potential for significant CDD/CDF emissions if it is equipped with a dry particulate matter control device (e.g., fabric filter or electrostatic precipitator) with an inlet gas temperature within the range of 450 to 750 °F, or if it is an industrial furnace that has hydrocarbon levels exceeding 20 ppmv. See §266.104(f)(2).

Dispersion modeling must be conducted in conformance with EPA's Guideline on Air Quality Models (Revised), EPA's "Hazardous Waste Combustion Air Quality Screening Procedure" provided in Methods Manual for Compliance with the BIF Regulations, or "EPA SCREEN Screening Procedure" as described in Screening Procedures for Estimating Air Quality Impact of Stationary Sources. All three documents are incorporated by reference in today's final rule at §260.11. To evaluate potential cancer risk from the CDD/CDF congeners, prescribed procedures must be used to estimate the 2,3,7,8-TCDD toxicity equivalence of the 2,3,7,8-chlorinated congeners. See "Procedure for Estimating Toxicity Equivalent of Chlorinated Dibenzo-p-dioxin and Dibenzofuran

U.S. EPA, "Report of the Products of Incomplete Combustion Subcommittee of the Science Advisory Board", Report # EPA-SAB-EC-90-004, January 1990.

EPA is not requiring that the estimated cancer risk from CDD/CDF be added to the risk from metal emissions to demonstrate that the summed risk to the maximum exposed individual is less than 10<sup>-5</sup>. The Agency believes that it is inappropriate to sum the estimated health risk from metals that are known or probable human carcinogens with a toxicity equivalency factor for CDD/CDF that is designed to be very conservative.

Congeners" in <u>Methods Manual for Compliance with the BIF Regulations</u> incorporated in the rule by reference in §260.11(a).

Studies conducted by the Agency<sup>40</sup> and others<sup>41</sup> during development of regulations for municipal waste combustors (MWCs) concluded that PM control devices operated at temperatures greater than 450°F have the potential for emitting elevated levels of CDD/CDF. At these temperatures, precursor organic materials and chlorine in the flue gas can be catalyzed by PM captured in the PM collection device to form CDD/CDF. Based on these findings, the Agency proposed to restrict the combustion of hazardous waste in BIFs that operate with PM control device temperatures greater than 450°F.

A number of commenters opposed the proposed limitation on the flue gas temperature to less than 450°F. Several commenters pointed out technical distinctions among types of boilers and industrial furnaces that affect the ability of a unit to change flue gas temperature and the potential of an ESP to form CDD/CDF. For example, many boiler and industrial furnaces either combust wastes that are very low in chlorine or that have high levels of chlorine capture within the process (e.g., cement kilns). As a result, the CDD/CDF emission potential will vary for different boilers and industrial furnaces, as well as between boilers and industrial furnaces and MWCs. Commenters also stated that there is no direct evidence of CDD/CDF emissions from several types of boilers and industrial furnaces, and that compliance testing to demonstrate 99.99 percent DRE of POHCs and continuous monitoring of CO and HC levels is adequate to ensure minimal emissions of organic compounds.

The Agency has reviewed the available data on the theory of CDD/CDF formation as well as CDD/CDF emissions from BIFs. Based on this review, the Agency agrees that most, but not necessarily all, BIFs burning hazardous waste have low CDD/CDF emission rates. For example, EPA recently tested a cement kiln burning hazardous waste that operates with an ESP at a temperature of 500-550°F and found it to have relatively high CDD/CDF emissions.<sup>42</sup> (EPA conducted a risk assessment, however, that estimated the

See U.S. EPA, "Municipal Waste Combustion Study: Combustion Control of Organic Emissions", EPA/530-SW-87-021C, NTIS Order No. PB87-206090; U.S. EPA, "Municipal Waste Combustion Study: Flue Gas Cleaning Technology", EPA/530-SW-87-021D, NTIS Order No. PB87-208108; and 54 FR 52251 (December 20, 1989).

Vogg H. and L. Stieglitz, "Thermal Behavior of PCDD/PCDF in Fly Ash from Municipal Waste Incinerators", Chemosphere, pp. 1373-1378, 1986.

U.S. EPA, Emissions Testing of a Wet Cement Kiln at Hannibal, MO, December 1990.

increased lifetime cancer risk to the hypothetical maximum exposed individual from the CDD/CDF emissions ranged from 7 in 10,000,000 to 2 in 1,000,000 without burning hazardous waste and from 2 in 1,000,000 to 4 in 1,000,000 when burning hazardous waste, well under the 1 in 100,000 limit established in today's rule.) The Agency suspects that the elevated CDD/CDF concentrations in the stack gas at this cement kiln are the result of the ESP's operating temperature and the level of HC precursor material in the flue gas. HC concentrations ranged from 66 to 70 ppmv (measured with a hot system, reported as propane, and corrected to 7% oxygen, dry basis) without hazardous waste burning and from 38 ppmv to 63 ppmv with hazardous waste burning. (We note that to continue burning hazardous waste under today's rule, the Director must establish during the Part B permit proceedings an alternative HC level for this kiln based on a demonstration by the applicant that HC levels are not higher when burning hazardous waste than under normal conditions and that the facility is designed and operated to minimize HC emissions from all sources -- fuels and raw materials. At certification of compliance with the emissions controls other than the HC limit, this facility must also propose a HC concentration limit for the remainder of interim status (until that limit or another limit is established under permit proceedings) that will ensure that HC levels when hazardous waste is burned will not be higher than baseline levels (i.e., HC levels when the system is designed and operated to minimize HC emissions from all sources, when burning normal fuels and feeding normal raw materials to produce normal products, and when not burning hazardous waste)). In addition, trial burn emissions testing must demonstrate that emissions of organic compounds are not likely to result in an increased lifetime cancer risk to the hypothetical maximum exposed individual exceeding 1 in 100,000. See §266.104(f) and discussion in section II.B.5.b of Part Two of this preamble.) There may be other factors that influence CDD/CDF levels at this facility (and other facilities), but this is uncertain. In addition, the exact HC concentration in combustion gas below which elevated CDD/CDF concentrations will not occur is unknown.

The Agency continues to believe that the operating temperature of the PM control device (and HC concentrations in flue gas) plays a significant role in CDD/CDF emissions. For a given HC concentration in the flue gas, the available data suggest that the potential for elevated CDD/CDF emissions is low if the PM control device operates at temperatures of less than 450°F or above 750°F. Consequently, today's rule does not require BIFs with PM control devices operating at temperatures outside of the 450-750°F window to determine CDD/CDF emission rates (unless it is an industrial furnace with HC levels greater than 20 ppmv). Owners and operators of units operating within the temperature

window, however, are required to conduct stack testing to determine CDD/CDF emission rates and to conduct a risk assessment using prescribed procedures to demonstrate that the estimated increased lifetime cancer risk to the hypothetical maximum exposed individual is less than 1 in 100,000.

The Agency notes that the final rule for municipal waste combustors (MWCs) may take a slightly different approach to control dioxin and furans by limiting temperatures at the inlet of the PM air pollution control system to within 30°F of those achieved in a dioxin/furan compliance test. The preamble to that rule, however, will probably continue to note the possibility of dioxin/furan formation in the temperature range of 230°C (450°F). In today's rule, the Agency believes that using temperature and HC levels as a trigger to dioxin/furan testing and risk assessment will be fully protective of human health and the environment and somewhat easier to implement than the MWC approach.

# III. Risk Assessment Procedures

The Agency uses assessment of health risk to develop and implement the final rules for metals, hydrochloric acid (HCl), and chlorine gas (Cl<sub>2</sub>). Specifically, the Agency has used risk assessment to: (1) establish ambient air concentrations of Appendix VIII compounds that do not pose an unacceptable health risk for purposes of this rulemaking; and (2) establish risk-based, conservative feed rate and emissions Screening Limits for metals and HCl. In addition, if facilities fail the Screening Limits or elect to conduct dispersion modeling to obtain less conservative limits, the rule allows facilities to use site-specific dispersion modeling to establish emission limits, and ultimately feed rate limits for metals and chlorine.

To establish health-based acceptable ambient concentrations for noncarcinogenic toxic metal and nonmetal compounds (except for HCl, Cl<sub>2</sub> and lead), EPA converted oral reference doses to reference air concentrations (RACs) by assuming average breathing volumes and body weights, and by applying a safety and a background level factor. See 54 FR at 43756. Health-based concentrations for carcinogenic pollutants were derived by converting cancer potency factors, or slopes (unique for each carcinogen), into Risk Specific Doses (RSDs) at a risk level of 1 in 100,000.<sup>43</sup> Since carcinogens are assumed to

We note that the cancer risk from the carcinogenic metals must be summed to ensure that the summed risk is not greater than 1 in 100,000. Thus, when more than one carcinogenic metal is emitted, the allowable ground level concentration for each carcinogenic metal is less than the 10<sup>-5</sup> Risk Specific Dose for that metal.

pose a small but finite risk of cancer even at very low doses, the RSD reflects a certain risk level, corresponding to 1 chance in 100,000, or  $10^{-5}$  excess risk of cancer for the maximally exposed individual if exposed continuously to multiple carcinogenic chemicals for a 70-year lifetime. RACs for HCl and Cl<sub>2</sub> are based on inhalation data, and a RAC for lead is based on the National Ambient Air Quality Standard (NAAQS).

To establish the Screening Limits for metals and HCl, air dispersion modeling was applied to back-calculate maximum acceptable feed rates and stack emissions rates from risk-based, acceptable ambient concentrations. These calculations were performed for various terrain types, effective stack heights, and land use classifications. The resulting permissible Screening Limits reflect plausible, reasonable worst-case assumptions about a generic facility that are not site-specific. The Screening Limits process provides a rapid and convenient risk-based mechanism to determine compliance. Conservative assumptions used to estimate health impacts exposure in the Screening Limit process include: (1) use of reasonable, worst-case estimate of dispersion of stack emissions; and (2) for the Tier I feed rate Screening Limits, assuming that all metals and chlorine fed into the BIF in all feedstreams are emitted (i.e., there is no partitioning to bottom ash or product, and not removal by an air pollution control system).<sup>44</sup> See 52 FR 17002 (May 6, 1987) and 54 FR 43729 (October 26, 1989).) Thus, assumptions and the Screening Limits tend to err intentionally on the side of protecting human health.<sup>45</sup>

If emission levels exceed the Screening Limits, (or if the owner/operator so elects) the rule allows a facility to conduct its own site-specific air dispersion modeling in order to establish metals, HCl, and Cl<sub>2</sub> emission limits. Incorporation of site-specific information allows less conservative assumptions (than the reasonable worst-case, nonsite-specific defaults), to be used in the dispersion models. Consequently, site-specific air dispersion modeling may predict lower ambient concentrations than the nonsite-specific modeling reflected in the Screening Limits, thus allowing higher emissions and feed rate limits.

To obtain credit for partitioning to residue or product and for APCS removal efficiency, owners and operators must conduct emissions testing to demonstrate the overall System Removal Efficiency (SRE) -- partitioning plus APCS removal efficiency. The Agency has not assumed an SRE in developing the Tier 1 feed rate Screening Limits because there are many site-specific factors that can affect the SRE.

We note that the Screening Limits may not always be conservative, however. Today's rule identifies criteria whereby the Screening Limits may not be used because they may not be conservative. See §266.106(7). That paragraph in the rule also gives the Agency authority to determine whether the Screening Limits may not be protective in a particular situation. In that case, the owner and operator must use the Tier III procedures -- site-specific dispersion modeling.

## A. Health Effects Data.

1. Carcinogens. Health effects evaluations for carcinogens have been summarized in Part Three, I. D, "Evaluation of Health Risk" in the April 27, 1990 proposal (see 55 FR 17873). To summarize briefly, in contrast to noncarcinogens, carcinogens are assumed to present a small but finite risk of causing cancer, even at very low doses. The slope of the dose-response curve in the low dose region is assumed to be linear for carcinogens. Because of this, the slope of the curve in the low dose region may be used as an estimate of carcinogenic potency. The unit risk is defined as the incremental lifetime risk estimated to result from exposure of an individual for a 70-year lifetime to a carcinogen in air containing 1 microgram of the compound per cubic meter of air (ug/m³). At an air concentration of 1 ug/m³, the cancer potency slope is numerically equivalent to the unit risk. Thus, at a preselected risk level, the corresponding air concentration which would cause that risk may be calculated by dividing the desired risk level by the unit risk value. Although the resulting value represents an air concentration with units of ug/m³, this concentration is referred to as the Risk Specific Dose (RSD).

When exposed to more than one carcinogen, the Guidelines for Carcinogenic Risk Assessment (51 FR 33992 (September 24, 1986)) recommend adding risks from the individual carcinogens to obtain the aggregate risk (i.e., cancer risks from exposure to more than one carcinogen are assumed to be additive). For today's rule, the Agency has proposed that an aggregate risk level for metals (i.e., arsenic, beryllium, cadmium, and hexavalent chromium) of 10<sup>-5</sup> is appropriate because it would limit the risk level for individual carcinogens to the order of 10<sup>-6</sup>. The Agency points out, however, that in selecting the appropriate risk level for a particular regulatory program, it considers such factors as the particular statutory mandate involved, nature of the pollutants, control alternatives, fate and transport of the pollutant in different media, and potential human exposure. See, e.g., 54 FR at 38049 (Sept. 14, 1989). Particular factors bearing on the Agency's choice here include the wide array and potentially large volumes of carcinogenic pollutants that can be emitted by these devices (unlike the situation in such rules as the benzene NESHAP when a single pollutant with well-understood effects was at issue), the need to guard against environmental harm as well as harm to human health, potential synergistic effects of the carcinogens emitted by these devices (which effects are not accounted for by the risk assessment), and legislative history indicating Congressional preference for parity of regulation between BIFs burning hazardous waste fuels and hazardous waste incinerators (S. Rep. No. 284, 98th Cong. 1st Sess. 38)). In addition, the increased recognition of the need to control net air emissions of toxic pollutants generally, manifest in Title III of the Clean Air Act Amendments of 1990, influences the Agency's choice of a conservative risk target in this rule. These same factors can also influence choice of a risk level where the Agency is making site-specific determinations.

The following section discusses comments on health effects data on carcinogens.

a. Unit Risk Factors/Risk Specific Doses. A few commenters argued for deletion of category C carcinogens from consideration in the risk assessment process.

Given that the carcinogenic metals arsenic, beryllium, cadmium, and hexavalent chromium are classified as either A or B carcinogens, this discussion pertains only to the C nonmetal Appendix VIII compounds for which the Agency established 10<sup>-5</sup> RSDs for purposes of implementing the low risk waste exemption, risk assessments for cement kilns with HC levels exceeding 20 ppmv, and health-based limits for Bevill excluded waste.

As a conservative element in the risk assessment process, and especially for purposes of implementing an exemption from some of the emission controls, EPA does not believe that exposure to category C carcinogens should be ignored at this time for those chemicals with cancer potency slopes. The classification schemes categorize chemicals based upon weight of the evidence, not carcinogenic potency. Therefore, a highly potent carcinogen may be classified in the C category and present a threat to health.

b. Quality of the Toxicological Data Base. Several commenters questioned the quality and extent of the toxicology data base and EPA's selection of specific studies used to calculate the cancer potency factors and unit risk values for a particular chemical. For example, one commenter noted that the molecular species of a metal compound emitted from an incinerator may be markedly different from the metallic complex actually tested for carcinogenicity and used to calculate that metal's cancer potency factor. This would distort the risk assessment process. This same commenter argued that beryllium oxide, which would be formed preferentially at the extreme temperatures of a furnace, is relatively inert compared to the molecular complex of beryllium which forms the basis of the cancer potency factor. Another commenter contended that, in general, the less water soluble (and, therefore, less bioavailable) metallic oxides are emitted from incinerators whereas the metallic species tested for cancer were more water soluble and bioavailable (i.e., absorbable into the organism).

EPA acknowledges the concern that the metal complex tested for carcinogenicity in animals reflect that to which humans are exposed. However, the particular metal complex being emitted may not have been tested in animals. In such cases, it is sometimes necessary to use that toxicological data which is available (on the same metal but complexed with a different ligand), limitations notwithstanding, until appropriate data on the complex of concern become available. EPA believes the use of the available data base will result in risk assessment methodology that is protective of human health and the environment.

Moreover, EPA notes that soluble metallic salts may also be emitted under some conditions (e.g., metallic chlorides). For screening purposes, the conservative assumption that soluble (i.e., bioavailable) metallic complexes are emitted, is assumed to protect health. For the site-specific risk assessment option, historical or test burn data may be used to identify probable emitted metallic species. If permit officials conclude during the permit process that appropriate fate, transport, and toxicological data exist for the actual emitted complex to support risk assessment, this could then be used in the site-specific risk assessment option.

c. High Dose to Low Dose Extrapolation. Several commenters questioned the scientific merit of extrapolating from high dose experimental data to low dose cancer risks using existing statistical models, asserting that the process is not biologically-based and is extremely conservative (i.e., overly health-protective). Two commenters asserted that the linearized multistage model should not be applied to non-genotoxic carcinogens because such "carcinogens" promote rather than initiate cancer, thus acting as a classical toxicant with a threshold. These commenters maintained that a chemical such as chloroform, which they claim is non-genotoxic (i.e., has not tested positive in mutation assays), would have a threshold below which there is no risk of cancer. Another commenter argued that biological evidence indicates a threshold for arsenic-induced cancer due to its known benefit as an essential trace element at low doses. This same commenter asserted that hexavalent chromium (Cr+6) is quickly converted in the body to the essential trace element Cr+3 and, therefore, should be treated as a "threshold carcinogen."

The Agency is following closely recent developments in scientific consensus regarding the basic molecular biology of cancer. EPA will revise its Guidelines for carcinogen risk assessment, and other guidance documents, to reflect developing scientific theory on high to low dose extrapolation threshold effects, and other related issues. Until

that time, EPA will continue to use its current approach, believing that a more conservative approach is warranted in the face of uncertainty.

d. Chromium Oxidation State. Several commenters argued that the current proposal does not differentiate chromium in the +6 oxidation state from chromium +3. They contend that most chromium emitted from boilers, industrial furnaces, and incinerators exists in the +3 state. Consequently, the proposed approach, which assumes that all chromium is +6, may overstate risks drastically. The commenters recommended that EPA assume that only a fraction of the chromium emitted by incinerators exists in the +6 oxidation state.

EPA concludes that assuming that 100% of the chromium is in the hexavalent oxidation state is a conservative assumption taken in the face of limited data. In a test<sup>46</sup> of hazardous waste incinerator emissions under varying levels of total chlorine in the waste burned, a high percentage of the total chromium emitted was in the hexavalent state under certain conditions. Until more data is available, showing consistently lower proportions of Cr<sup>+6</sup> under a variety of combustion conditions, EPA believes it is health-protective to assume that chromium from incinerator emissions exists in the hexavalent state. Facilities may elect to conduct emissions testing to determine the actual emission rate of Cr+6.

e. Additive Risks. One commenter criticized EPA's selection of 10<sup>-5</sup> as the acceptable aggregate risk level (for carcinogenic metals) for deriving screening limits, and claimed the selection is arbitrary and inconsistent with other EPA policy. EPA policy, the commenter notes, has traditionally embraced a range of risks from 10<sup>-7</sup> to 10<sup>-4</sup>, with the final EPA-selected risk level dependent upon site-specific conditions (i.e., characteristics and size of the exposed population).

EPA's rationale for selecting 10<sup>-5</sup> risk for the MEI is described in the October 26, 1989 supplemental notice (54 Federal Register 43754). In summary, EPA continues to believe that the aggregate cancer risk to the MEI of 10<sup>-5</sup> for metals is appropriate because: (1) it provides adequate protection of public health; (2) it considers weight of evidence of human carcinogenicity; (3) it limits the risk from individual Group A and B carcinogens to risk levels on the order of 10<sup>-6</sup>; and (4) it is within the range of risk levels the Agency has

U.S. EPA, "Pilot Scale Evaluation of the Fate of Trace Metals in a Rotary Kiln Incinerator with a Venturi Scrubber/Packed Column Scrubber, Vol. I, Technical Results", April 1989.

used for hazardous waste regulatory programs. See also the discussion in section III.A.1 of Part Three above.

2. Noncarcinogens. For toxic substances not known to display carcinogenic properties, there appears to be an identifiable exposure threshold below which adverse health effects usually do not occur. Noncarcinogenic effects are manifested when these pollutants are present in concentrations great enough to overcome the homeostatic, compensating, and adaptive mechanisms of the organism. Thus, protection against the adverse health effects of a toxicant is likely to be achieved by preventing total exposure levels that would result in a dose exceeding its threshold. Since other sources in addition to the controlled source may contribute to exposure, ambient concentrations associated with the controlled source should ideally take other potential sources into account. Therefore, the Agency has conservatively defined reference air concentrations (RACs) for noncarcinogenic compounds that are defined in terms of a fixed fraction of the estimated threshold concentration. The RACs for lead and hydrogen chloride, however, were established differently, as discussed below. The RACs established in today's final rule are identical to those proposed. (See Appendix H of the Supplement to Proposed Rule at 54 FR 43762 (October 26, 1989)). (The Agency notes that it does not intend for RACs to be used as a means of setting air quality standards in other contexts. For instance, the RAC methodology does not imply a decision to supplant standards established under the Clean Air Act.)

We note, however, that the RACs proposed in Appendix H of the supplement to proposed rule (and promulgated today as Appendix IV to the rule) included both Agency-verified and unverified values. Unverified values are subject to revision as the Agency's Reference Dose Workgroup continues to establish verified inhalation RfDs. (Occasionally, the Agency may also revise verified values based on new and significant information.) Since the supplemental notice, the Workgroup has established inhalation RfDs for eight compounds on proposed Appendix H (and promulgated Appendix IV to the rule). The basis for the newly-verified RfDs is set forth in the Health Effects Assessment Summary Tables. Fourth Quarter-FY90, U.S. EPA, OERR 9200 6-303 (90-4), September 1990.<sup>47</sup> Consequently, RACs based on those RfDs are different from the proposed and promulgated RACs. The RACs based on verified inhalation RfDs are shown in the table

The document is available from the National Technical Information Service (NTIS), 5285 port Royal Road, Springfield, VA 22161, (703) 487-4600. The document number is PB90-921-104.

below. EPA will use the omnibus permit authority of §270.32(b)(2) to use these revised RACs where the facts warrant.<sup>48</sup>

Compound	RAC in Appendix IV of Final Rule (ug/m <sup>3</sup> )	RAC Based on Recently- Verified RfD (ug/m <sup>3</sup> )
Acroelin (107-02-8)	20	0.03
Carbon Disulfide (75-15-0)	200	3
p-Dichlorobenzene (106-46-7)	10	200
Bromomethane (74-83-9)	0.8	2
Hydrogen Sulfide (7783-06-4)	3	0.2
Mercury (7439-97-6)	0.3	0.08
Methoxychlor (72-43-5)	50	4
Toluene (108-88-3)	300	500

RACs have been derived from oral reference doses (RfDs) for those noncarcinogenic compounds listed in Appendix VIII of 40 CFR Part 261 (except for lead, HCl, and Cl<sub>2</sub>) for which the Agency considers that it has adequate health effects data. An oral RfD is an estimate (with an uncertainty of perhaps an order of magnitude) of a daily oral dose (commonly expressed with units of mg/kg-day) for the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects, even if exposure occurs daily for a lifetime. Since these oral RfDs are subject to change, EPA will undertake rulemakings as necessary if the derivative RACs change in a way that affects the regulatory standard (see also the discussion of this issue in the Boiler/Furnace supplemental notice published on October 26, 1989 at 54 FR 43718). We note that, in the interim before any such rulemaking is complete, and as discussed above,

EPA notes that permit writers choosing to invoke the omnibus permit authority of §270.32(b)(2) to add conditions to a RCRA permit must show that such conditions are necessary to ensure protection of human health and the environment and must provide support for the conditions to interested parties and accept and respond to comment. In addition, permit writers must justify in the administrative record supporting the permit any decisions based on omnibus authority.

permit officials may use the omnibus permit authority<sup>49</sup> of the statute to consider revised health effects data in establishing permit conditions.

The Agency's rationale for using oral RfDs as a basis for RAC-derivation is described in 54 FR 43755 (October 26, 1989). EPA believes the approach to derive RACs is reasonable because: (1) the RfDs are verified by an EPA workgroup whose decisions are subject to public review; (2) the verification process addresses long term (lifetime) exposure; (3) the RfDs are based on the best available information meeting specific scientific criteria; (4) the most sensitive individuals are considered; and (5) the RfD determination takes into account the confidence in the quality of the information on which they are based. Nevertheless, the Agency's Inhalation RfD Workgroup is developing reference dose values (concentrations) for inhalation exposure for several chemicals, and some are currently available. As reference concentrations are established by the Workgroup, the Agency will consider the need to change the RACs established in today's rule as discussed above.

The final rule regulates HCl emissions based on an annual exposure (long-term) RAC of 7 ug/m<sup>3</sup>.<sup>50</sup> The RAC is based on the threshold of priority effects resulting from exposure to HCl. Background levels were considered to be insignificant given that there are not many large sources of HCl and that this pollutant generally should not be transported over long distances in the lower atmosphere.

The Agency also proposed a short-term (i.e., 3-minute exposure) RAC for HCl. The Agency agrees with commenters, however, that the proposed RAC was not technically supportable. See discussion in section V of Part Four of this preamble. Consequently, the final rule does not establish a short-term RAC for HCl.

To consider the health effects from lead emissions, we adjusted the National Ambient Air Quality Standard (NAAQS) by a factor of one-tenth to account for background ambient levels and indirect exposure from the source in question. Thus, although the lead NAAQS is 1.5 ug/m<sup>3</sup>, for purposes of this regulation, sources could contribute only up to

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<sup>50</sup> U.S. EPA, Integrated Risk Information System (IRIS) Chemical Files.

0.15 ug/m<sup>3</sup>. Given, however, that the lead NAAQS is based on a quarterly average, the equivalent annual exposure is 0.09 ug/m<sup>3</sup>.

Finally, section 109 of the Clean Air Act (CAA) requires EPA to establish ambient standards for pollutants determined to be injurious to public health, allowing for an adequate margin of safety. Secondary NAAQS, also authorized by section 109, must be designed to protect public welfare in addition to public health, and, thus, are more stringent. As discussed above, the Reference Air Concentration (RAC) used in today's rule for Lead is based on the Lead NAAQS. As the Agency develops additional NAAQS for toxic compounds that may be emitted from hazardous waste incinerators, we will consider whether the acceptable ambient levels (and, subsequently, the feed rate and emission rate Screening Limits) ultimately established under this rule should be revised. We note again that the reference air concentration values (and risk-specific dose values for carcinogens) presented here in no way preclude the Agency from establishing NAAQS as appropriate for these compounds under authority of the CAA.

a. Derivation of Oral RfDs/RACs. Many commenters responded to the issue of derivation of oral RfDs/RACs, questioning the scientific basis for the oral RfDs and conversion of RfDs to RACs. Some commenters stated that use of oral RfDs do not factor in differences in routes of exposure (e.g., absorption, first-pass effects) when extrapolating from oral to inhalation routes of exposure. As discussed above, we acknowledge the limitations of developing RACs from oral RfDs but continue to believe the approach used is reasonable and the best available approach until the Agency's Inhalation RfD Workgroup can provide inhalation values.

Other commenters directed their comments exclusively to lead, indicating that the lead RAC was arbitrary. EPA has based the lead RAC on the National Ambient Air Quality Standard (NAAQS). This was done in part because no reference dose or cancer potency slope is currently available for this metal. The final rule uses 10%, rather than 25% as is used for other compounds, as an apportionment factor (as proposed) because the Agency is particularly concerned with: (1) the possible high contribution of lead exposure by indirect pathways, particularly in urban environments; and (2) the growing concern of low level lead exposure in children since the lead NAAQS was established. (The Agency currently plans to propose to readjust the lead NAAQS in 1991.)

b. Apportionment. Some commenters questioned EPA's proposal apportioning 75% of the RfD to other non-specified sources, thus causing the RAC to correspond to

25% of the RfD. The commenters indicated that the figure of 75% from other sources was arbitrary and could vary from one chemical to another. They suggested that unless other sources of exposure were identified, the RAC should reflect 100% of the RfD.

EPA has chosen a fraction (25%) of the RfD to serve as the basis for the RACs because indirect pathways, known to contribute to risks, are not quantified in these regulations. Even apart from exposures contributed by sources separate from the boiler, industrial furnace, or incinerator, indirect pathways from emissions from these devices themselves may contribute 75% or more to risk. Such indirect (i.e., non-inhalation) pathways include deposition of emitted chemicals on: (1) gardens and crops directly consumed by humans; (2) meadows used for grazing by beef cattle and other edible livestock; and (3) meadows and fodder used by dairy cattle (and subsequent milk consumption by humans).

Such real exposures, which are not quantified in these rules, are accounted for by the allowance for 75% contribution from other sources. Moreover, it is questionable whether any single facility should be allowed to consume 100% of an individual's exposure allowance, above which any further exposure might cause adverse health effects.

## B. Air Dispersion Modeling

The Agency used air dispersion modeling to develop the Screening Limits and dispersion modeling is available as the exposure assessment component of the site-specific risk assessment option. A more extensive discussion of air dispersion modeling is included in the 1989 supplemental notice (see 54 FR 43752-54). This discussion focuses on derivation of Screening Limits, wherein the dispersion models are used to "back-calculate" emission rates from acceptable ground level concentrations. The section is also applicable to dispersion modeling used for the risk assessment option (where ground level concentrations are predicted from estimated emissions rates). The reader is referred to this discussion for further information about air dispersion modeling. It should be noted that for the purposes of the risk assessment option, more site-specific information may be used in place of some of the conservative default assumptions used to derive the Screening Limits, generally resulting in lower predicted ambient air concentrations.

1. Option for Site-Specific Modeling. In responding to this provision in the proposal, many commenters argued for procedures which would allow greater flexibility in the air dispersion modeling process. Many commenters seemed to confuse the issues of

dispersion modeling used for the Screening Limits, and modeling for the site-specific risk assessment. EPA concedes that many assumptions used to develop the Screening Limits are, by design, conservative to ensure that the Limits are protective in most cases. These assumptions do not apply, however, when an owner or operator conducts site-specific dispersion modeling under the Tier III standards. For site-specific dispersion modeling, procedures specified in EPA's Guideline on Air Ouality Models must be used.

2. Terrain-Adjusted Effective Stack Height. Two commenters stated that in adjusting the stack height to account for local terrain and differentiating for terrain in the screening limits, EPA is "double counting" the influence of terrain unnecessarily. One commenter added that such terrain adjustment of stack height is not supported by the current EPA Guideline on Air Quality Models (Revised) and should be eliminated.

EPA acknowledged this "double counting" of terrain in the supplement to the proposed rule (54 FR 43759), stating that this additional conservatism is necessary to account for the wide range of terrain complexities encountered at real facilities. EPA continues to believe that this double counting is necessary. Without this conservatism, additional criteria would have to be added to the existing list (see §266.106(b)(7)) for determining when the screening limits may not be conservative and, thus, may not be used. Commenters did not propose (and provide support for) additional criteria for determining when the use of less conservative screening limits would be appropriate. Further, EPA believes that additional criteria would complicate and delay the implementation of the rule by placing additional burden on regulatory officials. Moreover, if a facility cannot meet the screening limits, then site-specific dispersion modeling may be used to demonstrate compliance with the Tier III standards. Detailed, comprehensive dispersion modeling generally costs less than \$5,000 and, thus, should not pose a substantial burden. In fact, many BIFs have already conducted such modeling to comply with applicable standards under the Clean Air Act. Finally, the final rule minimizes the burden of dispersion modeling by allowing the use of screening models.

3. Conservatism in Screening Limits. Five commenters stated that EPA's approach to setting the screening limits is overly conservative and illustrated this by calculating the difference in estimated ground level concentrations using site-specific information as opposed to the default assumptions recommended for the Screening Limits.

It should be noted that the Agency would expect that the use of site-specific information would lead to higher emission limits that under the screening limits. However,

the Agency developed feed rate and emission rate screening limits with the intent of minimizing the need for site-specific dispersion modeling and thus reducing the burden of demonstrating compliance with the emissions standards. To ensure that the limits are protective in most cases, however, the Agency derived the limits using conservative assumptions. The Agency believes that, although the assumptions are reasonable, they would likely limit emissions by a factor of 2 to 20 times lower than would be allowed by site-specific dispersion modeling (54 FR 43758).

4. GEP Stack Height. Two commenters stated that EPA should not impose a GEP stack height limitation for existing stacks. The commenters went on to state that EPA should allow modeling of emissions at actual stack height for existing stacks or, at a minimum, adopt a grandfather provision to exclude GEP from applying to stacks constructed prior to December 31, 1970. One commenter also indicated that EPA should recognize that the stack height used for conducting a site-specific dispersion modeling analysis may exceed GEP formula height, as allowed under Section 123 of the Clean Air Act.

The Agency maintains that in complying with the metals and HCl/Cl<sub>2</sub> controls credit will not be allowed for stack heights greater than GEP. GEP stack heights are determined in a manner consistent with the <u>Guideline for Determination of Good Engineering Practice Stack Height</u> (Technical Support Document for the Stack Height Regulations), Revised (EPA 450/480-023R).

EPA's position here is consistent with the prohibition on using physical stack height in excess of GEP in the development of emission limitations under EPA's Air Program at 40 CFR 51.12 and 40 CFR 51.18. Stack heights higher than GEP cannot be used for compliance purposes because such stacks merely provide added dispersion and dilution of ambient levels. EPA prefers that pollutants be removed from the stack gas to avoid build-up of persistent pollutants (e.g., metals) in the environment and subsequent indirect exposure through, for example, the food chain. In addition, better dispersion of emissions of carcinogenic compounds can merely expose larger populations to (albeit lower) concentrations of pollutants and may not decrease the aggregate population risk (i.e., cancer incidents/year in the affected population).

5. Plume Rise Table. One commenter recommended that EPA extend Table F-2 (plume rise) and Tables E-1 through E-10 (feed rate and emissions screening limits) of the October 26, 1989 supplemental notice to account for the high flow rates typical of many

cement plant stacks. Another commenter stated that the effective stack height of most utility boilers exceeds the maximum stack height contained in Tables E-1 through E-10. One commenter indicated that the plume rise values presented in Table F-2 are not conservative for conditions of neutral atmospheric stability at average to high wind speeds or for stable atmospheric conditions at all typical wind speeds. This commenter added that the screening limits based on Table F-2 plume rise may not be conservative for regions having complex terrain.

For the final rule, the plume rise values presented in Table F-2 of the supplement to the proposed rule were revised and the table was expanded to include higher stack exit flow rates indicative of cement kiln stacks (exit flow rates were increased up to a level of 200 m<sup>3</sup>/s). See Appendix VI to the final rule. The plume rise table values were originally developed based on plume rise equations presented in the 1979 User's Guide to the Industrial Source Complex (ISC) model. The plume rise formulation in the ISC model has since been changed to correspond to the way other EPA models determine plume rise. Consequently, the entire table was revised, based on conservative application of the updated neutral and stable buoyant plume rise equations.<sup>51</sup> The revised values of plume rise represent the lowest value of conservative stable buoyant and neutral buoyant plume rise for each flow rate/temperature level.

The range of terrain-adjusted effective stack heights, shown in Tables E-1 through E-10 of the supplemental notice, was not increased beyond the height of 120 meters. This height was determined to be the maximum terrain-adjusted effective stack height based on the stack parameter and site location data used in the development of the dispersion coefficients (as described in Appendix F of the proposed, supplemental rule). Facilities with terrain-adjusted effective stack heights that exceed 120 meters have the option of conducting site-specific dispersion modeling to demonstrate compliance.

6. Compliance by Manipulating Effective Stack Height. One commenter claimed that facilities may elect to circumvent compliance by manipulating their effective stack heights. This commenter added that additional exposures could result from the increased dispersion from taller stacks. The Agency acknowledges that an owner or operator could increase physical stack height up to the GEP maximum to achieve better dispersion and hence a higher allowable emission rate. The Agency maintains, however, that it is more

Memorandum from Sue Templeman, Radian Corp., to Dwight Hlustick, EPA, entitled "Derivation of Plume Rise Values for BIFs", dated November 30, 1990.

protective of human health and the environment (see discussion in section III.B.4 above) and it may be more cost-effective to upgrade emission control equipment to state-of-the-art control, rather than to increase stack height, particularly given that the Agency plans to consider in the future whether additional controls are needed to better control metals emissions. See discussion in section section I of Part Three of this preamble.

7. Effect of HCl Emissions on Acid Rain. One commenter disagreed with the use of Screening Limits for HCl which are based solely upon effective stack height, terrain and land use. This commenter maintained that this approach ignores the effects of HCl in atmospheric reactions and acid rain.

Addressing potential effects of HCl in atmospheric reactions and acid rain is beyond the scope of this rule. The screening limits were developed to protect human health in the vicinity of facilities burning hazardous waste.

8. Building Wake Effects. One commenter stated that emissions limits based on effective stack height, terrain, and land use would not be conservative in cases where stacks are subject to building wake effects. This commenter added that only consideration of building wake effects will lead to conservative concentrations for stacks influenced by nearby structures and recommended that site-specific dispersion modeling be required in all cases where the "Guideline for Air Quality Models (Revised)" indicates the necessity for consideration of building wake effects.

The development of the conservative dispersion coefficients incorporated an eleventh hypothetical source in order to represent facilities whose release heights do not meet good engineering practice and whose plumes would thus be subject to building wake effects (54 FR 43752). In addition, the Agency acknowledges that the dispersion coefficients used to establish the Tier I and II Screening Limits may not be conservative in extremely poor dispersion conditions or when the ambient-air receptor is located close to the source and has therefore defined five situations for which the permit writer should require site-specific dispersion modeling (54 FR 43754). Furthermore, the Agency is reserving the right to require that a site-specific dispersion modeling analysis be conducted, irrespective of whether the facility meets the specific Screening Limits. Thus, the permit writer has the option of overruling use of Tier I or II, if a probability exists that application of this methodology would not be protective of the health-based standards. The Tier III approach of conducting site-specific dispersion modeling requires incorporation of building wake effects, as necessary, in the modeling analysis. The Tier I and II Screening Limit

methodology was not further modified to account for these factors, as it already embodies repeated use of conservative assumptions.

### C. Consideration of Indirect Exposure and Environmental Impacts

1. Indirect Exposure. During the proposal stages of these regulations, a few commenters recommended incorporating indirect exposure pathways into the risk assessment process. Indirect exposure is defined, in these regulations, as any exposure pathway other than direct inhalation of emissions from a boiler or industrial furnace. One commenter maintained that emissions such as metals, chlorinated dioxins, and furans would be environmentally persistent and able to enter the food chain after deposition on the ground (including crops, pasture land, surface waters). Consequently, the commenter argued that indirect exposures should be factored into the risk assessment.

EPA recognizes that the contribution of indirect pathways may be significant. However, the Agency believes that other conservative procedures, such as apportioning 75% of exposures to either indirect pathways or other emission sources (that can contribute to background levels) in the calculation of RACs, will help offset the contribution of indirect pathways. Another significant source of conservatism, offsetting the contribution of indirect pathways, is represented by the inherent uncertainty, and consequent conservatism, in the models used to estimate unit risk values. Use of the MEI in the Screening Limits procedure comprises yet another conservative element in the risk assessment process which would offset direct estimation of indirect pathway exposure. Therefore, the Agency has not modified the risk assessment process to address indirect pathways.

2. Non-human Health Related Environmental Impacts. One commenter noted that for many pollutants, environmental standards for certain flora and fauna may be more stringent than for humans. Therefore, the effect on non-human receptors should not be ignored in the regulations and the environmental risks should be evaluated.

EPA is concerned about the potential effects of BIF emissions on non-human receptors. While some environmental standards are available for the protection of environmental receptors (notably EPA water quality criteria for aquatic organisms), methods for quantifying exposure and defining acceptable levels for non-human receptors are still largely in the developmental stages. Thus, until these critical procedures are better established, the Agency is not requiring such an evaluation at this time. However, as noted

earlier, some of the conservatism in the human health risk assessment is designed to compensate for the absence of direct environmental standards.

## D. Acceptable Risk Level for Carcinogens

Today's rule limits the incremental lifetime cancer risk to the hypothetical maximum exposed individual (MEI) to  $10^{-5}$ . This risk level is within the range of levels historically used by EPA in its hazardous waste and emergency response programs --  $10^{-4}$  to  $10^{-6}$ .

Under the rule, we are limiting the <u>aggregate</u> risk to the MEI from carcinogenic metals to  $10^{-5}$ , and the <u>aggregate</u> risk from carcinogenic organic compounds (dioxins and furans and other PICs under provisions of the alternative HC limit) to  $10^{-5}$ . This will limit in most cases the risk from <u>individual</u> carcinogenic compounds to levels on the order of  $10^{-6}$  but below  $10^{-5}$ . The rule does not require that the risk from carcinogenic organic compounds be added to the risk from carcinogenic metals. This is because the Agency does not believe it is appropriate to sum the risk from metals (i.e., arsenic, beryllium, cadmium, and chromium) that are known or probable human carcinogens (Group A or B carcinogens under the weight-of-evidence approach) with the risk from organic compounds, many of which are possible human carcinogens (Group C carcinogens).

In selecting a 10<sup>-5</sup> aggregate risk threshold level for this rule, we considered risk thresholds in the range of 10<sup>-4</sup> to 10<sup>-6</sup>, the range the Agency generally uses for various aspects of its hazardous waste programs.

We considered limiting the aggregate risk to the MEI to  $10^{-6}$  but determined that this risk threshold would be unnecessarily conservative for the purpose of this rule. In reaching this determination, we considered that, at an aggregate risk level of  $10^{-6}$ , the risk level for individual metals would be on the order of  $10^{-7}$ , which we believe is overly conservative for this rule.

Alternatively, we considered limiting the aggregate risk to the MEI to  $10^{-4}$ . An aggregate risk threshold of  $10^{-4}$  would result in limiting the risk level for individual carcinogens on the order of  $10^{-5}$ . We did not select a  $10^{-4}$  aggregate risk threshold for this proposed rule for a number of reasons. In selecting the appropriate risk level for a particular regulatory program, the Agency considers such factors as the particular statutory mandate involved, nature of the pollutants, control alternatives, fate and transport of the pollutant in different media, and potential human exposure. The Agency believes that a  $10^{-5}$  risk level is appropriate for this rule because: (1) the rule limits emissions considering

only direct exposure via inhalation of dispersed emissions. Other routes of exposure (e.g., soil ingestion, uptake through the food chain) are not accounted for by this methodology, which means the risk is somewhat higher; (2) the carcinogenic metals that the rule controls are Group A or B (i.e., known or probable) human carcinogens; (3) we are concerned about the potential risks posed by the unknown pollutants these devices can emit -- i.e., products of incomplete combustion (PICs).<sup>52</sup>; and (4) the 10<sup>-5</sup> risk level does not result in a rule that poses a substantial burden on the regulated community given that it is neither a major rule as defined by Executive Order 12291 nor will it significantly impact small entities.

When the proposed regulations were published and comments were solicited from affected parties, several commenters responded to the issue of acceptable risk levels for exposure to carcinogens. These commenters questioned the basis of  $10^{-5}$  as representing an acceptable risk level. They maintained that the discussion in the rule, serving as the rationale or justification for selecting this level of risk, was inadequate. Others asserted that the selected acceptable level of cancer risk was not consistent with other regulations (specifically,  $10^{-4}$  cancer risk to the MEI was used to set a national emission standard (NESHAP) for benzene, and  $10^{-5}$  for individuals living "some distance from the source").

The Agency continues to believe that the aggregate cancer risk to the MEI of  $10^{-5}$  is appropriate here because: (1) it provides adequate protection of public health; (2) it limits the risk from individual Group A and B carcinogens to risk levels on the order of  $10^{-6}$ ; and (3) it is within the range of risk levels the Agency has used for hazardous waste regulatory programs. See also discussion in section III.A above.

#### E. Use of MEI/Consideration of Aggregate Risk

The Agency considered the use of aggregate population risk or cancer incidence (i.e., cancer incidents per year) in developing the national emission limits and in site-specific risk assessments. This approach could, in some situations, be more conservative than considering only MEI risk because, even if the "acceptable" MEI risk level were not exceeded, large population centers may be exposed to emission such that the increased cancer incidence could be significant. However, it would be difficult to develop acceptable aggregate cancer incidence rates. Nevertheless, it is likely that many facilities that perform

This rule is, thus, unlike the Benzene NESHAP where EPA targeted one known pollutant with known effects.

a site-specific MEI exposure and risk analysis would also generate an aggregate population exposure and risk analysis that could be considered by the Agency.

Several commenters addressed the issue of using the maximum exposed individual (MEI) as a basis for risk estimation and recommended using population (aggregate) risks as a more realistic alternative. They maintained that health risks are overstated if based only on exposure of the Maximum Exposed Individual (MEI). Aggregate population-based exposures, which are usually much lower would more realistically represent site-specific health risks. Many commenters noted that using the MEI exposure implicitly assumes that population risks are similar.

EPA believes that evaluation of the MEI only (and not aggregate population risk) is usually a conservative feature of the risk assessment. For screening purposes, a simplified approach is necessary. While site-specific demographic data is usually readily available from 1980 census data, its incorporation into a screen would complicate the screening process unnecessarily. Calculation of screening limits based on the risk to the MEI requires much less site-specific information, facilitating application of the screen to a broad range of sites. If the facility does not meet the screening limits, the option of site-specific risk assessment is still available. While MEI exposures are estimated routinely in a site-specific risk assessment, aggregate population risks may also be estimated, if desired.

Several commenters also contended that even the risk estimates for the MEI may be overly health-protective since the MEI is assumed to reside at this high exposure location 24 hours per day, 365 days per year, for a 70-year lifetime. A more fair evaluation of MEI risk would account for the attenuating effects of time spent indoors and off-site, and include estimates of average residence times and facility lifetimes. Moreover, some exposure assessments assume the MEI is located at the point of maximum ground level concentration predicted by the dispersion model, when in fact, no one may live at this site.

EPA acknowledges that use of the hypothetical MEI is a conservative feature of the rule but maintains that it is reasonable to balance against the potentially nonconservative features of the rule discussed below.

#### F. Risk Assessment Assumptions

As indicated in the above discussion, we have used a number of assumptions in the risk assessment, some conservative and others nonconservative, to simplify the analysis or to address issues where definitive data do not exist.

# Conservative assumptions include the following:

- Individuals reside at the point of maximum annual average ground level concentrations. Furthermore, risk estimates for carcinogens assume that the maximum exposed individual resides at the point of maximum annual average concentration for a 70-year lifetime.
- Indoor air contains the same levels of pollutants contributed by the source as outdoor air.
- For noncarcinogenic health determinations, background exposure already amounts to 75% of the RfD. This includes other routes of exposure, including ingestion and dermal. Thus, the BIF is only allowed to contribute 25% of the RfD via direct inhalation. The only exception is for lead, where a BIF is only allowed to contribute 10% of the NAAQS. This is because ambient lead levels in urban areas already represent a substantial portion (e.g., one-third or more) of the lead NAAQS. In addition, the Agency is particularly concerned about health risks from lead in light of health effects data available since the lead NAAQS was established. EPA is currently reviewing the lead NAAQS to determine if it should be lowered.
- Risks are considered for pollutants that are known, probable, and possible human carcinogens.
- Individual health risk numbers have large uncertainty factors implicit in their derivation to take into effect the most sensitive portion of the population.

Nonconservative assumptions include the following:

- For carcinogenic compounds, indirect routes of exposure are not considered, such as uptake of arsenic, beryllium, cadmium, and chromium through the food chain.
- Although emissions are complex mixtures, interactive effects of threshold or carcinogenic compounds have not been considered in this regulation because data on such relationships are inadequate.
- Environmental effects (i.e., effects on plants and animals) have not been considered because of a lack of adequate information. Adverse effects on plants and animals may occur at levels lower than those that cause adverse human health effects. (The Agency is also developing procedures and requesting Science Advisory Board review to consider environmental effects resulting from emissions from all categories of waste combustion facilities.)

Many commenters responded broadly on the impact of assumptions and uncertainty in risk assessment. While generally supporting the concept of risk assessment, some asserted that EPA's proposed assumptions were too conservative regarding estimated emission levels, dispersion modeling, and health impact estimation. Further, they maintained that assumptions were not well enough justified and the conservative bias used for each of the multiple assumptions required in a risk assessment tends to accumulate,

resulting in gross over-estimation of health impacts. Some of the specific assumptions that commenters considered too conservative are discussed in the following paragraphs.

Two commenters asserted that emission control technology should not be assumed absent when estimating emission levels. One commenter recommended that sensitivity analysis be incorporated into the risk assessment process. This commenter also recommended incorporation into the risk assessment of population mobility (i.e., time spent away from the site), facility lifetimes less than 70 years, and an attenuation factor for time spent indoors, rather than assume 24 hr/day, 70-year exposure.

Many of the respondents argued that economic impacts resulting from overly-conservative risk assessments are substantial. To avoid some of the default assumptions is also burdensome in the commenters judgment, requiring trial burns, emissions measurements, slag and product assays, and detailed air quality dispersion modeling.

Although many of the assumptions discussed by the commenters are conservative in nature, it is difficult to determine how less conservative assumptions could be used in light of the considerable associated uncertainty. Much of the conservatism referred to originates from assumptions used to derive screening levels. When screening levels are derived, either: (1) no site-specific information is available (nor may be assumed if the procedure is intended to screen a variety of sites); or (2) incorporation of site-specific information in the derivation of screening levels would so complicate the process as to render it prohibitively time-consuming and defeat its utility as a screen. Thus, in light of the uncertainty (i.e., no site specific information), conservative assumptions are used to derive the screening limits that EPA believes to be protective of human health and the environment.

If the facility fails to meet the screening criteria, the option of site-specific risk assessment is still available. For site-specific risk assessment, more realistic and less conservative assumptions may be incorporated, reflecting actual site or facility conditions.

### V. Controls for Emissions of Toxic Metals

The Agency has identified 12 toxic metals in Appendix VIII of 40 CFR Part 261 that may pose a hazard to human health and the environment: antimony, arsenic, barium, beryllium, cadmium, hexavalent chromium, lead, mercury, nickel, selenium, silver, and thallium. Five of these metals (or their compounds) are known or suspected carcinogens: arsenic, beryllium, cadmium, hexavalent chromium, and nickel.

Many of these toxic metals are contained in hazardous waste that is burned in boilers and industrial furnaces. Many hazardous waste fuels contain metals at levels orders of magnitude higher than levels found in No. 6 fuel oil. Metal-bearing wastes typically used as fuel in boilers and industrial furnaces include spent halogenated and nonhalogenated degreasing solvents used for metals cleaning, paint manufacturing wastes, and other organic liquid wastes with high heating values. Currently, metals emissions from the burning of these wastes are not controlled under RCRA for boilers and the types of industrial furnaces that burn hazardous wastes. Emissions of carcinogenic metals can potentially result in increased lifetime cancer risks of greater than 1 x 10<sup>-4</sup> and emissions of noncarcinogenic metals such as lead can result in ambient levels that result in adverse health effects.

Today's final rule promulgates the controls as discussed in the October 1989 supplement to the proposed rule (see 54 FR 43728-29).<sup>53</sup> See §266.106. The rules establish metals emission limits for 10 toxic metals<sup>54</sup> listed in Appendix VIII of 40 CFR Part 261 based on projected inhalation health risks to a hypothetical maximum exposed individual (MEI). The standards for the carcinogenic metals (arsenic, beryllium, cadmium, and chromium) limit the increased lifetime cancer risk to the MEI to a maximum of 1 in 100,000. The risk from the four carcinogens must be summed to ensure that the combined risk is no greater than 1 in 100,000. The standards for the noncarcinogenic metals (antimony, barium, mercury, silver, and thallium) are based on Reference Doses (RfDs) below which adverse health effects have not been observed. The standard for lead is based on the National Ambient Air Quality Standard (NAAQS) for lead.

The owner and operator must analyze the hazardous waste to be burned and comply with the standard for each of the 10 metals that could reasonably be expected to be in the

Given time constraints in developing the final rule for promulgation, response to major comments could not be provided in the preamble. Responses to comments are provided in the Comment Response Document for the BIF Regulation.

As proposed the rule document limits and the rule document for the BIF Regulation.

As proposed, the rule does not limit emissions of nickel and selenium (see 54 FR 43729). Limits cannot be established for selenium because the Agency has inadequate health data to establish a reference air concentration. Nickel is not controlled because the two nickel compounds suspected at this time of being potential human carcinogens, nickel carbonyl and subsulfide, are not likely to be emitted from combustion devices, given their highly oxidizing conditions. In the 1989 supplemental notice to the proposed rule, EPA requested comments on whether the reduced carcinogenic forms of nickel were likely to be emitted from hazardous waste burning devices, especially those furnaces that may not use highly oxidized conditions. However, the Agency did not receive any comments on this issue pertinent to boilers and industrial furnaces.

waste. The metals excluded from analysis must be identified and the basis for their exclusion explained to ensure that there is adequate justification for not analyzing for a particular metal.

The standards are implemented through a three-tiered approach. Compliance with any tier is acceptable. The tiers are structured to allow higher emission rates (and feed rates) as the owner or operator elects to conduct more site-specific testing and analyses (e.g., emissions testing, dispersion modeling). Thus, the feed rate limits under each of the tiers are derived based on different levels of site-specific information related to facility design and surrounding terrain. Under Tier I (see §266.106(b)), the Agency has provided conservative waste feed rate limits in reference tables as a function of effective stack height and terrain and land use in the vicinity of the stack. The owner or operator demonstrates compliance by waste analysis, not emissions testing or dispersion modeling. Consequently, the Tier I feed rate limits are based an an assumed reasonable, worst-case dispersion scenario, and an assumption that all metals fed to the device are emitted (i.e., no partitioning to bottom ash or product, and no removal by an air pollution control device (APCD)).

Under Tier II (see §266.106(c)), the owner or operator conducts emissions testing (but not dispersion modeling) to get credit for partitioning to bottom ash or product, and APCD removal efficiency. Thus, the Agency has developed conservative emission rate limits in reference tables, again as a function of effective stack height and terrain and land use in the vicinity of the stack. The Agency also assumed reasonable, worst-case dispersion under Tier II.

Under Tier III (see §266.106(d)), the owner or operator elects to conduct emissions testing and site-specific dispersion modeling to demonstrate that the actual (measured) emissions do not exceed acceptable levels considering actual (predicted) dispersion.

The metals controls apply both to facilities applying for a Part B operating permit and to facilities operating during interim status. See section VII of Part Three of this preamble for discussion of how the standards apply during interim status.

### A. Background Information.

The following sections summarize EPA's regulation of metals emissions from boilers and industrial furnaces under other statutes, the 1987 proposed rule and comments

received on that proposal, and the basis for the 1989 revision to the proposed rule and comments received on that revised approach.

1. Metals Standards Under Other Statutes. As discussed below, EPA has promulgated standards applicable to boilers and industrial furnaces under other statutes for some but not all of the 10 toxic metals controlled by today's rule. Under the Clean Air Act (CAA), EPA established National Emissions Standards for Hazardous Air Pollutants (NESHAPS) for arsenic, beryllium, and mercury for certain categories of sources (40 CFR Part 61). These emission standards were developed considering the quantities and types of metals emissions from various source categories, current control practices, and the economic impacts of reducing emissions. In addition, EPA has established National Ambient Air Quality Standards<sup>55</sup> (NAAQS) for lead and particulate matter. These ambient standards are implemented by states under the State Implementation Plan (SIP) program to control major sources of lead and particulate emissions. The Agency does not believe that lead emissions standards have been established under the SIPs for any boilers and for many industrial furnaces that burn hazardous waste fuels (e.g., cement and light-weight aggregate kilns) because they are not major lead emitters as defined under the NAAQS. Therefore, EPA believes that today's metals controls are not redundant to existing Agency standards, and, thus, are necessary to ensure adequate protection of human health and the environment.

Particulate emission standards, however, established under the SIPs in conformance with the particulate NAAQS, or by EPA as New Source Performance Standards (NSPS), do apply to some boilers and industrial furnaces that burn hazardous waste. The particulate standards generally limit metals emissions to the extent that state-of-the-art particulate control technologies will allow. High efficiency electrostatic precipitators (ESPs) or fabric filters are usually required to meet these standards. However, these particulate emission standards may not adequately control metals emissions from the burning of hazardous wastes in many boilers and industrial furnaces for several reasons: (1) the particulate standards do not apply to gas and oil-fired boilers (which represent a large number of hazardous waste fuel burners); (2) smaller coal-fired boilers are not subject to NSPS standards and may not be required under the SIPs to be equipped with ESPs or fabric filters; (3) large volumes of hazardous waste fuels are burned by light weight

We note that the reference air concentration values for noncarcinogens and riskspecific dose values for carcinogens established by today's rule are not intended to, and in no way, preclude the Agency from establishing NAAQS as appropriate for these compounds under authority of the Clean Air Act.

aggregate kilns that are equipped with low-pressure wet scrubbers that may not be highly efficient at collecting particulates in the less than 1 micron range, the size range that contains the bulk of the particulate metals; and (4) the risks posed by metals emissions from these boilers and industrial furnaces that are equipped with ESPs, fabric filters, and wet scrubbers can increase substantially when hazardous waste fuel is burned since the levels of some metals, particularly chromium and lead, can be much higher in hazardous waste than in coal.

2. 1987 Proposed Rule. The 1987 proposed rule would have established a four-tiered standard to control emissions of arsenic, cadmium, hexavalent chromium, and lead. Each Tier represented a standard protective on its own, and demonstration of compliance with any Tier would have been sufficient. Tiers I through III established hazardous waste metals concentrations, feed rates, and emission screening limits, respectively, as a function of device type and thermal capacity. Tier IV would have provided for site-specific dispersion modeling to demonstrate that, when the screening limits were exceeded, emissions would nevertheless not pose an unacceptable health risk. Data available to the Agency indicated that only four of the 12 toxic metals listed in Appendix VIII of Part 261 were likely to be present in hazardous waste burned in boilers and industrial furnaces at levels posing a significant health risk. The permit writer would have determined on a case-by-case basis if any of the other toxic metals were present at levels posing a significant risk.

Public comments submitted on the 1987 proposal stated that EPA's database on the metals composition of hazardous waste was both limited and out of date in light of the Agency's data collection efforts at that time and the HSWA statutory requirement to pretreat waste that heretofore had been land disposed. As a result of HSWA, more hazardous waste is being burned, and pretreatment operations are often likely to involve combustion. The hazardous waste burned currently and in the future in boilers and industrial furnaces may include toxic metals other than the four targeted for regulation in the 1987 proposal. Therefore, the Agency requested comment in the October 1989 supplemental notice on expanding the list of regulated metals to include all 10 Appendix VIII metals. (Nickel and selenium were not included as discussed above.) In addition, if standards for all of the toxic metals were included in the rule, the burden on permit writers would actually be reduced because explicit standards would be provided for all metals of potential concern. Without explicit standards, permit writers would have to rely on the omnibus permit authority of the statute to add permit conditions as necessary to protect human health and

the environment. Using the omnibus permit authority can involve a lengthy and cumbersome interaction between permit officials and the applicant.

- 3. 1989 Supplement to Proposed Rule. Based on public comments submitted on the 1987 proposed rule and on additional evaluation of the risk assessment approach used for the proposal, the Agency discussed in the 1989 supplemental notice whether to (1) expand the list of metals for which emissions standards would be established in the rule to include all the toxic metals listed in Appendix VIII of Part 261 (except nickel and selenium, for the reasons discussed above); (2) establish the screening limits as a function of effective stack height, terrain, and land use rather than as a function of device type and capacity; and (3) rather than provide the screening limits in the rule itself as proposed in 1987, provide them in a guidance document that would be entitled "Risk Assessment Guideline (RAG) for Permitting Hazardous Waste Thermal Treatment Devices".
- a. Expanded List of Metals. In the 1989 supplemental notice, EPA proposed to expand the list of metals for which emissions standards would be established in the rule to include antimony, arsenic, barium, beryllium, cadmium, hexavalent chromium, lead, mercury, silver, and thallium. Thus, of the 12 toxic metals listed in Appendix VIII, only selenium and nickel would not be controlled for reasons discussed above. Today's final rule establishes standards for all 10 metals. We note that the controls apply only to metals that are present in the hazardous waste feed at detectable levels using procedures specified in SW-846. See §266.106(a).
- b. Revised Basis for Screening Limits. In the 1989 supplemental notice, EPA also proposed to revise the bases for the feed rate and emission rate screening limits to correlate them with stack height and terrain and land use in the vicinity of the facility because these parameters more directly relate emission controls to key parameters that affect the dispersion of emissions, and ultimately, ambient levels (i.e., more so than the proposed approach of correlating the screening limits to device type and heat input capacity). When developing the Tier I through Tier III screening limits proposed in 1987, the Agency made a simplified assumption that effective stack height correlated with thermal capacity (e.g., if the thermal capacity of one device was 10 percent greater than the thermal capacity of another, the effective stack height was also 10 percent greater). The Agency acknowledges that this assumption may not always hold. Stack height is often more a function of the height of nearby buildings and surrounding terrain than a function of the heat input capacity of the device. Thus, the final rule correlates the Tier I and Tier II screening limits to stack height, terrain, and land use.

c. Establishing the Screening Limits in the Rule. As originally proposed in 1987, the final rule incorporates the Tier I feed rate screening limits and the Tier II emissions rate screening limits in the rule itself rather than in a separate guidance document. Our concern (and many commenters concurred) is that a guidance document would not carry the weight of a regulation -- permit writers would be free to accept or reject the guidance (i.e., in this case, the screening limits and the reference air concentration (RACs) and risk-specific dose (RSD) values used to develop the limits). In addition, permit writers would be obligated to justify use and appropriateness of the guidance on a case-by-case basis. This would place a substantial burden on the permit writer and result in inconsistent, and perhaps, inappropriate permit conditions. Finally, implementing the emission standards during interim status as required by the final rule would be virtually impossible without incorporating the screening limits and RACs and RSDs in the rule.

We note that revisions to the RACs and RSD values will undoubtedly need to be made over time as the Agency obtains additional health effects information on the regulated pollutants, and corresponding revisions to the screening limits, will be made by formal rulemaking (i.e., proposed revisions, opportunity for public comment, and promulgation of final revisions). In the interim, however, permit writers may apply stricter limits than contained in the rule (if the facts justify it) pursuant to the omnibus permit authority<sup>56</sup> in Section 3005(c)(3).

In the 1989 proposal, as a possible alternative to monitoring waste feed rates and compositions, EPA requested comment on using the results of analyses of emission control residues to monitor compliance with the metals emission standards. Several commenters supported this approach. The final rule allows for this or other alternative approaches to implement the metals controls. See section V.C.4 of Part Three of the preamble.

#### B. How the Standards Work.

1. Tier III Standards. Tier III standards are discussed first because the Agency believes that the majority of facilities will elect to comply with these standards rather than

EPA notes that permit writers choosing to invoke the omnibus permit authority of §270.32(b)(2) to add conditions to a RCRA permit must show that such conditions are necessary to ensure protection of human health and the environment and must provide support for the conditions to interested parties and accept and respond to comment. In addition, permit writers must justify in the administrative record supporting the permit any decisions based on omnibus authority.

the Tier I or Tier II screening limits to obtain more flexible permit limits. The Tier III standards (see §266.106(d)) require: (1) emissions testing to determine actual emissions taking into account partitioning of metals to combustion gas versus ash or product; and removal of metals from flue gas by the air pollution control system (APCS); and (2) site-specific dispersion modeling to take into account actual, predicted dispersion conditions at the facility.

To comply with the Tier III standards, predicted ambient concentrations of the carcinogenic metals, arsenic, beryllium, cadmium, and hexavalent chromium at the hypothetical maximum exposed individual (MEI) may not result in an increased cancer risk of more than 1 in 100,000. The risk from each metal must be summed to ensure that the summed risk does not exceed 1 in 100,000. As proposed, the final rule establishes a risk-specific dose (RSD) for each metal at the  $10^{-5}$  (i.e., 1 in 100,000) risk level. If a person is exposed to the  $10^{-5}$  RSD (an ambient air concentration) over a lifetime, the probability of increased cancer incidence is not expected to exceed 1 in 100,000. To ensure that the summed risk from the four carcinogens is no greater than 1 in 100,000, the ratios of the predicted ambient concentration to the  $10^{-5}$  RSD must be summed for all metals to demonstrate that the sum does not exceed 1.0.57

For the noncarcinogenic metals, antimony, barium, mercury, silver, and thallium, predicted MEI ambient air concentrations may not exceed the reference air concentrations (RACs), as proposed. The RAC for lead is based on 10% of the National Ambient Air Quality Standard (NAAQS) for lead, as proposed. One commenter stated that the lead RAC may be appropriate for facilities in urban areas but that it is not appropriate for rural areas with low background lead levels. This commenter suggested a waiver of the lead RAC where a facility can show that measured ambient air lead levels do not exceed the NAAQS. Although this approach is reasonable, the final rule does not include a waiver provision for the lead RAC based on site-specific ambient air monitoring<sup>58</sup> because: (1)

To implement the metals controls, metals feed rates are limited to levels during the compliance test or trial burn. Thus, if the owner/operator would like to have the flexibility to burn wastes with varying (higher) levels of carcinogenic metals, he/she may choose to develop two or more operating modes with varying feed rates of carcinogenic metals. If so, a compliance test or trial burn would be required for each mode of operation to demonstrate that the summed risk from the carcinogenic metals does not exceed 1 in 100,000. Under this approach, the operator is required to identify the mode of operation at any time, and to comply with the metal feed rate limits for that mode of operation.

We note, however, that EPA's <u>Guideline on Air Quality Models</u> allows the use of ambient air monitoring to develop site-specific dispersion models.

the lead NAAQS may not be protective given that the Agency has been developing for some time a proposal to lower the NAAQS (perhaps by as much as 50%) based on health effects data obtained since the NAAQS was established initially (the Agency plans to propose a lower lead NAAQS in the fall of 1991); (2) the time and cost of conducting ambient monitoring in conformance with procedures established by EPA's Office of Air Quality Planning and Standards (OAQPS) would make this approach impracticable; (3) a waiver provision would add extra complexity to the rule; and (4) such a waiver could make eventual further regulation under amended section 112 of the Clean Air Act more likely.

- a. Emissions Testing. Stack emissions testing for metals must be conducted in conformance with "Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes" (Multiple Metals Train) provided in section 3.1 of Methods Manual for Compliance with the BIF Regulations (incorporated by reference in §260.11).
- b. Dispersion Modeling. Dispersion modeling must be conducted in conformance with EPA's Guideline on Air Quality Models (Revised), EPA's "Hazardous Waste Combustion Air Quality Screening Procedure" provided in Methods Manual for Compliance with the BIF Regulations, or "EPA SCREEN Screening Procedure" as described in Screening Procedures for Estimating Air Quality Impact of Stationary Sources. All three documents are incorporated by reference in today's final rule at §260.11. The Guideline on Air Quality Models is the Agency's primary guide for dispersion modeling. The "Hazardous Waste Combustion Air Quality Screening Procedure" is included in EPA's Guidance on Metals and Hydrogen Chloride Controls for Hazardous Waste Incinerators, Draft Final Report, August 1989. The derivation of this procedure, which was developed specifically for hazardous waste combustion facilities, is also included in that document. The data base used in the derivation is the same as that used for deriving the Tier I and Tier II screening limits as summarized in the October 26, 1989 supplement to the proposed BIF rule (54 FR 43752). Finally, the EPA SCREEN screening procedure has been in general use since 1988 when it was developed by EPA's Office of Air Quality Planning and Standards. It has been used by Regional Offices, States, and sources for air dispersion modeling required by EPA air regulations.

If a user determines that there is an inconsistency between either of the screening procedures discussed above and EPA's <u>Guideline on Air Quality Models</u>, the Guideline shall have primacy.

- c. GEP Stack Height. As proposed, stack heights used to demonstrate conformance with the final rule may not exceed Good Engineering Practice (GEP) as defined in 40 CFR Part 51.100(ii).
- d. MEI. As proposed, the hypothetical MEI concentration is the maximum annual average ground level concentration at an off-site location. On-site MEI locations need not be used to demonstrate conformance with the standards, unless a person resides on-site.
- e. Bubble Approach for Multiple Stacks. Given that the standards for metals (and HCl and Cl<sub>2</sub>) are health risk-based, the final rules are implemented using a limited "bubble" approach as proposed. Under the limited bubble approach, emissions from all hazardous waste combustion stacks at a facility subject to metals and chlorine feed rate limits must be considered in demonstrating conformance with the acceptable ambient levels. This includes all boilers and industrial furnaces regulated under today's rule, and also those RCRA-regulated incinerators and thermal treatment units where feed rate or emission limits have been established for metals, chlorine, HCl, or Cl<sub>2</sub> by EPA. (The Agency considered expanding the bubble to consider other stack emissions such as from nonhazardous waste incinerators or process stacks, but believes that effective implementation would be difficult given the different types and levels of regulatory control and procedures applicable to a variety of stack emission sources.)

To implement the bubble approach, dispersion modeling must consider emissions from all regulated stacks (see discussion above) to predict the maximum annual average off-site ground level (i.e., MEI) concentration of each metal. The MEI location will generally vary for each metal.

2. Tier II Standards. See §266.106(c). The final rule incorporates the Tier II emission rate screening limits (see Appendix I of the final rule) as presented in the 1989 supplemental notice as a function of terrain adjusted effective stack height, and noncomplex versus complex terrain and urban versus rural land use in the vicinity of the facility. The limits were back-calculated from the RACs and 10<sup>-5</sup> RSDs established by today's rule using reasonable, worst-case dispersion scenarios. Conformance with the Tier II emission rate screening limits is demonstrated by emissions testing (i.e., the facility's actual emissions are compared to the maximum allowable screening limits).

The methodologies for determining terrain adjusted effective stack height and terrain type are established in §§266.106(b)(3) and (4), and the methodology for determining land

use in the vicinity of the stack are provided in "Simplified Land Use Classification Procedures for Compliance with Tier I and Tier II Limits in Appendix VI of Methods Manual for Compliance with the BIF Regulations (incorporated by reference in today's rule, see §260.11).

- a. Special Requirements for Carcinogens. We note that the Tier II emission rate screening limits for the carcinogenic metals arsenic, beryllium, cadmium, hexavalent chromium, are back-calculated from the 10<sup>-5</sup> RSD for each metal. Thus, if the actual emission rate of one of those metals was at the Tier II screening limit, the resulting risk to the MEI is estimated to be 1 in 100,000. Given that the rule requires that the summed risk for all carcinogenic metals cannot exceed 1 in 100,000, the ratios of the actual emission rate to the Tier II allowable emission rate for all of the carcinogenic metals must be summed and the sum cannot exceed 1.0.
- b. Bubble Approach for Multiple Stacks. Although we believe that most facilities will use Tier III dispersion modeling to demonstrate conformance with the metals (and HCl and Cl<sub>2</sub>) controls when they have multiple stacks to obtain credit for actual dispersion conditions, Tier II (or Tier I) may be used. To use the Tier I feed rate limits or Tier II emissions rate limits for multiple stacks, the owner/operator must conservatively assume that all hazardous waste is fed to the source with the worst-case stack (i.e., considering dispersion). The worst-case stack must be determined from the following equation<sup>59</sup> as applied to each stack:

K = HVT

where:

K = a parameter accounting for relative influence of stack height and plume rise;

H = physical stack height (meters);

 $V = flow rate (m^3/second);$  and

T = exhaust temperature (Kelvin).

The stack with the lowest value of K must be used as the worst-case stack.

c. Facilities Ineligible to Use the Tier II (and Tier I) Screening Limits. The screening limits were back-calculated from the RACs and 10<sup>-5</sup> RSDs established by today's rule using dispersion modeling scenarios that the Agency considers reasonable,

This equation was proposed at 54 FR 43762 (Oct. 26, 1989). It is derived from a similar equation on pp. 2-3 of Screening Procedures for Estimating Air Quality Impact of Stationary Sources, EPA-450/4-88-010, August 1988.

worst-case dispersion scenarios. However, dispersion characteristics at a particular facility may, in fact, provide worse dispersion of emissions than used to calculate the screening limits. Consequently, the final rule, as discussed in the 1989 supplemental notice, establishes criteria for facilities that are ineligible to use the screening limits. See §266.107(b)(7).

3. Tier I Standards. See §266.106(b). The final rule incorporates the Tier I feed rate screening limits (see Appendix I to the rule) as presented in the 1989 supplemental notice as a function of terrain adjusted effective stack height, and noncomplex versus complex terrain and urban versus rural land use in the vicinity of the facility. Conformance with the Tier I feed rate screening limits is demonstrated by sampling and analysis of all feed streams (hazardous waste, other fuels, and raw materials).

By complying with the conservative Tier I feed rate screening limits, applicants burning hazardous waste with very low concentrations of metals would not have to conduct emissions testing. The feed rate limits are back-calculated from the emission screening limits, assuming that all metals present in feedstreams are emitted to the atmosphere. Thus, no metals are assumed to partition to the bottom ash or product, and no allowance is made for removal of metals from the stack gas by an air pollution control system. Consequently, the Tier I feed rate screening limits are equivalent to the Tier II emission rate screening limits and are provided in the same table in Appendix I to the rule. (At proposal, the feed rate and emission rate screening limits were provided in separate tables because the Agency presented the limits in different units -- lb/hr (pound per hour) for feed rate limits, and g/s (grams per second) for emission rate limits. To avoid confusion and for simplicity, however, the final rule combines the Tier I and II screening limits and presents the limits in g/hr (grams per hour)).

The Tier II discussions above on special requirements for carcinogens also applies to the Tier I feed rate limits. Thus, to demonstrate conformance with the feed rate limits for the carcinogenic metals, the sum of the ratios of the actual feed rate to the Tier I allowable feed rate for all of the carcinogenic metals must be summed, and the sum cannot exceed 1.0.

In addition, the Tier II discussions above on the bubble approach for multiple stacks and criteria for facilities that are ineligible to use the screening limits apply to the Tier I feed rate screening limits as well.

Finally, we note that the Tier I feed rate limits may be adjusted upward to reflect site-specific dispersion modeling. This is a hybrid of Tiers I and III. See §266.106(e). Under this approach, site-specific dispersion modeling may be conducted using the procedures discussed above to back-calculate allowable emission rates for each metal. These allowable emission rates then become the adjusted feed rate limits. Given that emissions testing is not conducted under this modified Tier I approach, no credit is given for partitioning of metals to bottom ash or product, or removal by the air pollution control system.

#### C. Implementation.

As discussed above, EPA developed a three-tiered standard to ensure that metals emissions do not pose an unacceptable risk to human health and the environment. Tier I consists of conservative feed rate screening limits, Tier II establishes conservative emission rate screening limits, and Tier III allows the use of site-specific air dispersion modeling to demonstrate compliance. The decision of which tier to use depends on the physical characteristics of the facility and surrounding terrain, on the anticipated waste compositions and feed rates, and on the level of resources available for conducting the analysis. It is acceptable to use different tiers to comply with the standards for different metals.

- 1. Tier I Implementation. The Tier I feed rate limits are implemented by sampling and analysis as necessary and flow rate monitoring of each feedstream (i.e., hazardous waste, other fuels, and raw materials) to ensure that the total feed rate of each metal does not exceed the Tier I limit on either an hourly rolling average or instantaneous basis (i.e., at any time), except as provided for the carcinogenic metals and lead as discussed below.
- a. Special Procedures for Carcinogenic Metals. Given that, for the carcinogenic metals, the sum of the ratios of the actual feed rates to the Tier I allowable feed rates cannot exceed 1.0, there are no fixed feed rate limits for individual carcinogenic metals. Rather, the operator must insure that on an hourly rolling average or instantaneous basis (or as allowed below for carcinogenic metals and lead) that the mixture of carcinogenic metals fed into the BIF does not exceed allowable levels. To demonstrate conformance with this standard, the operator must: (1) know the concentration of metals in each feedstream and the flow rate of each feedstream; (2) calculate on an hourly rolling average or instantaneous basis (or as allowed below for carcinogenic metals and lead) the sum of the ratios of the actual feed rate to the allowable feed rate; and (3) ensure that the sum of the ratios for all

carcinogenic metals (on an hourly rolling average or instantaneous basis or as allowed below) does not exceed 1.0.

b. Averaging Periods. As discussed in the 1989 supplemental notice, the final rule provides an alternative averaging period to the hourly rolling average or instantaneous basis for the carcinogenic metals arsenic, beryllium, cadmium, and chromium, and for lead. For these metals, an averaging period not to exceed 24 hours (i.e., 24-hour rolling average) may be used provided that the feed rate at any time (i.e., instantaneously) does not exceed 10 times the feed rate on an hourly rolling average basis. The Agency believes that an averaging period greater than an hourly rolling average is reasonable given that the metals controls are based on lifetime exposures. However, the Agency is concerned that averaging periods greater than 24 hours may be difficult to enforce. A ten-fold higher emission rate should not pose adverse health effects from short-term exposures for the carcinogenic metals because the 24-hour rolling average would not exceed the level that could pose a 10<sup>-5</sup> health risk over a lifetime of exposure and the threshold (i.e., noncancer) health effect would not be likely at exposures only ten times higher than the  $10^{-5}$  RSD. A ten-fold higher instantaneous ambient level for lead should not pose adverse health effects given that the acceptable ambient level for long-term exposure to lead (i.e., the lead RAC) is based on only 10% of the National Ambient Air Quality Standard.

We do not believe that a similar approach for the other noncarcinogenic metals would be appropriate given the uncertainty in the level of protection provided by the long-term acceptable ambient levels (e.g., the RACs are based on oral RfDs converted 1 to 1 to inhalation values).

- 2. Tier II Implementation. Conformance with the Tier II emission rate screening limits is based on emissions testing (see section IV.B.1.a) using the Multiple Metals Train prescribed in Methods Manual for Compliance with the BIF Regulations (incorporated by reference in §260.11(a)). The Tier II emission limits are implemented by permit limits on the following parameters based on operations during the trial burn:
  - Maximum feed rate of each metal in total feedstreams (e.g., hazardous waste, raw material, other fuel), except as discussed below;
  - Maximum feed rate of each metal in total hazardous waste feedstreams:
  - Maximum feed rate of each metal in all pumpable hazardous waste feedstreams;

- Maximum feed rate of total hazardous waste and pumpable hazardous waste;
- Maximum feed rate of chlorine in total feedstreams;
- Maximum capacity in appropriate units (e.g., total heat input, pounds of steam produced, raw material feed rate);
- Maximum temperature at the inlet to the air pollution control system (APCS);
- Maximum combustion chamber temperature; and
- Key parameters to ensure proper operation of the APCS.

The approach that must be used to measure these parameters and the approach to establish limits on each parameter based on trial burn data is specified in §266.102(e)(6).

In addition, the permit must specify sampling and analysis procedures for all feedstreams and all flow rates of all feedstreams must be continuously monitored and recorded.

The final rule establishes limits on these parameters because they can affect metals emissions. The feed rate of metals in both total hazardous waste feeds and pumpable hazardous waste feeds is limited because the physical form of the waste (e.g., solid vs liquid) can affect the partitioning of the metal between bottom ash (for a boiler) or product (for a furnace) and combustion gas entering the PM control system. Metals partition to the combustion gas more readily when fired in a liquid or pumpable form.

The rule limits the metal feed rate from total feedstreams to account for metals in raw materials and nonhazardous fuels. When added to the emissions from hazardous waste, noncarcinogenic metals from these sources can cause the MEI concentration to exceed the threshold level for health effects and carcinogenic metals from these sources can cause the MEI concentration to exceed the incremental lifetime cancer risk limit for the rule of 1 in 100,000. Thus, there controls ensure that burning hazardous waste does not result in unacceptable risks.

The rule limits the chlorine feed rate because chlorine can increase the volatility of metals, thus increasing the rate of partitioning to the combustion gas and, in some cases,

resulting in smaller metal particulates in flue gas that can be more difficult to control with a PM collection system.

The rule limits the maximum capacity of the device to ensure that, during the compliance test (under interim status) or the trial burn (under a Part B permit application) the device is feeding raw materials and nonhazardous fuels at a rate that will not be exceeded after the compliance test or trial burn. Thus, the gas flow rate and particulate loading are maximized during the compliance test or trial burn, which tests the ability of the PM collection system to control metals.

The rule limits the maximum temperature at the inlet to the PM collection system because temperature affects the volatility of a metal -- some metal species may be partially (or totally in the case of mercury) in the vapor form at high temperatures at the inlet to the PM collection system which will reduce the amount of the metal collected. Limiting the inlet temperature to that occurring during the compliance test or trial burn will ensure that the temperature cannot be increased later which could result in an increase in metals emissions.

Finally, the rule limits key operating parameters of the PM air pollution control system to ensure that it continues to operate as efficiently as it did during the compliance test or trial burn.

- 3. Tier III Implementation. Conformance with Tier III is demonstrated by emissions testing and site-specific dispersion modeling showing that ambient levels of metals do not exceed allowable levels. Permit limits are established for the same parameters as required for Tier II.
- 4. Special Requirements for Furnaces that Recycle Collected Particulate Matter. Metal emissions are not feasibly monitored on a continuous basis. Thus, some other means of demonstrating compliance is necessary. For most types of BIFs, compliance is demonstrated by monitoring feed rates of metals from all feedstreams. EPA requested comment on whether approaches other than monitoring feed rates of metals may be more appropriate to implement the metals controls. See 54 FR 43760 (Oct. 26, 1989). A number of commenters argued that the material balance approach for implementing the metals controls was impractical and nonconservative for cement kilns. The material balance approach for metals limits the feed rate of each metal in three types of feeds: (1) pumpable hazardous waste; (2) total hazardous waste; and (3) total feedstreams. Although limiting

the feed rate of each metal in the total hazardous waste feed and the pumpable hazardous waste feed was workable, commenters argued that limiting the feed rate of metals in total feedstreams was impractical for cement kilns because of the variety of raw materials they feed. Raw materials to a cement kiln are a blend of several components including calcium sources such as limestone, sea shells, marl, or chalk, silica sources such as clay, shale, slate, or sand, and iron sources such as iron ore or mill grindings. The proportions of the components of the blend are changed frequently according to the type of cement desired and the composition of the sources. This can make it very difficult to accurately determine the metals feed rate in the blended raw materials.

Of even more concern to the Agency, however, is the fact that the material balance approach is not likely to be conservative (i.e., protective) for furnaces, like cement kilns, that recycle collected PM back into the furnace. Because the dust is recycled, an increase in the feed rate of a metal in one of the feedstreams — such as spiking during a compliance test (under interim status) or a trial burn (under a Part B permit application) — leads to a gradual increase in the concentration (and feed rate) of the metal in the recharged kiln dust which leads to a gradual increase in the metal emissions. Several recharge cycles may be necessary for the kiln to reach steady state condition. Thus, until the system reaches equilibrium, metals feed rates do not correlate with metals emissions.

EPA considered a number of alternatives to address the problem that the recycled dust creates a system that is out of equilibrium when a metal is spiked. We considered handling the recycled dust as another feedstream. Under this approach, the feed rate of metals in the recycled dust would be considered along with those from other feedstreams. (Or alternatively, the feed rate of metals in the recycled dust would be considered as a fourth level of metals feed rate controls -- that is, the feed rate of metals in pumpable hazardous waste, total hazardous waste, recycled dust, and total feedstreams would be limited.) We did not adopt this approach because: (1) the recycled dust is an internal recycled stream so that limits on the recycled dust coupled with limits on other feedstreams would probably correlate with metals emissions in the kiln off-gas, but not necessarily with stack emissions; and (2) during an emissions test when metals are spiked, the system will not be in equilibrium and we do not know enough about metal behavior in the system to determine whether the metals feed rate in the dust would be higher or lower after reaching equilibrium (i.e., we did not know whether this approach would be conservative).

To address this concern that the material balance approach to implementing metals controls is not likely to be conservative (i.e., protective) for furnaces that recycle dust,

today's rule requires owners and operators of such devices to comply with one of three alternatives: (1) daily monitoring of collected PM to ensure that metals levels do not exceed limits that relate concentration of the metal in the collected PM to emitted PM; (2) daily stack sampling for metals; or (3) conditioning of the furnace system prior to compliance testing to ensure that metals emissions are at equilibrium with metals feed rates. We discuss each of these procedures below.

We note first, however, that today's rule gives owners and operators the option of selecting one of these methods only during interim status. The Director will determine under the Part B permit application proceeding which of these methods (or whether another method) may be more appropriate on a case-by-case basis considering the facts. See §266.106(f). In addition, we note that experience with these methods during interim status may indicate the need to refine them for use under a RCRA operating permit. Finally, we note that this provision of the permit standards is not limited to furnaces that recycle collected PM. (However, the methods discussed below may be used during interim status only by furnaces that recycle collected PM.) The permit standards provide this flexibility because, although we believe that these methods (as they may be refined with experience) or other methods that adequately address the concerns described below must be required for systems that recycle collected PM, the first two methods (i.e., monitoring collected PM or daily stack sampling) may be preferable for other types of devices as well. This is because these first two alternative methods address not only the special problem caused by recycled PM but also the problem of the difficulty (and imprecision) associated with limiting metals emission rates by the material balance approach given the variability of waste and raw material matrices and variability of the concentrations of metals in feedstreams, a problem that also exists for these furnaces and will exist for other devices as well.60

a. Monitoring Metals in Collected PM. This approach will control metals emission rates by establishing limits on all of the parameters discussed above for implementing the Tier II and Tier III controls, except for limits on the feed rate of each metal in total feedstreams. In lieu of that parameter, the final rule limits the concentration of each metal in collected PM. See "Alternative Methodology for Implementing Metals Controls" in Method Manual for Compliance with the BIF Regulations (incorporated by reference in §260.11). The concentration limit is calculated by determining the maximum allowable

We also note that these methods may be preferrable to the material balance approach in some situations for implementing the metals controls for hazardous waste incinerators.

concentration of each metal in the emitted PM and by empirically relating the concentration of the metal in the emitted PM to the concentration of the metal in collected PM (i.e., the enrichment factor). The maximum allowable concentration of each metal in the emitted PM is determined by dividing the allowable emission rate for the metal in pounds per hour by the applicable PM standard<sup>61</sup> in pounds per hour. The enrichment factor (i.e., concentration of a metal in emitted PM divided by the concentration in collected PM) is determined initially by a series of 10 emissions tests over a two-week period. Quarterly testing is required thereafter to determine if the enrichment factor changes substantially. If so, the series of 10 emissions tests must be conducted again to establish the revised enrichment factor.

EPA acknowledges certain potential limitations to this approach: (1) the Agency has limited data to support the main assumption of this approach -- that the enrichment factor will remain constant over the range of normal operating conditions that occur between the initial series of 10 tests to establish the enrichment factor and the quarterly confirmation tests; and (2) that a problem with emissions is detected after the fact. However, we have built into the approach conservative features that should address concern about whether the enrichment factor may change over time. First, the approach assumes that the facility is always operating at its maximum allowable PM emission limit. Although allowable metal concentrations in collected PM would be higher when the facility operates at lower PM emission levels, the limits do not change. Thus, for example, for every 10% the facility operates under its PM standard, the limit on metals concentrations in collected PM are conservative (lower than necessary) by 10%. Second, the enrichment factor is statistically determined based on test data as the lower of: (1) twice the enrichment factor at the 95% confidence level; or (2) the enrichment factor at the 99% confidence level. Where there is significant scatter in the data, twice the enrichment factor at the 95% confidence level is likely to govern. Thus, when the enrichment factor varies significantly during the 10 tests, not only is the enrichment factor based on the 95% confidence level, but an additional margin of safety is provided by doubling the factor at the 95% confidence level for purposes of determining the metal limit in collected PM.62

The applicable PM standard is 0.08 gr/dscf or any more stringent standard that may apply under the NSPS or SIP.

In addition, the methodology requires that a "safe enrichment factor" of 100 be used when a metal is at nondetect levels in the collected PM. Mercury, for example, may be at nondetect levels because it is likely to be in the vapor form (and not collected as PM) in an ESP or baghouse.

As for detection after the fact, sampling of collected dust is required every eight hours to form a daily composite sample. The operator is allowed up to 48 hours to analyze the daily composite<sup>63</sup> given that the analytical procedures can take 24 to 48 hours even for on-site laboratories. In addition, if the sample fails the concentration limit for a metal, the operator may analyze two duplicate samples that he may have elected to obtain to determine if the failed sample is an outlier. Analyses of these back-up samples will also take up to 48 hours. Thus, it could take up to four days to confirm that a dust sample has failed the concentration limit and that a violation of the metals emissions controls may have occurred.<sup>64</sup>

Notwithstanding this provision of the method, EPA expects that owners and operators that want to comply with the spirit of the controls and to operate in a manner that is protective of human health and the environment will conduct triplicate analyses of samples for those metals that may exceed the "conservative" metal limit to avoid the time delay of subsequently analyzing back-up samples if the initial sample fails the concentration limit. Owners/operators should use historical data to determine whether a metal may be close to exceeding a concentration limit and, thus, routinely analyze "back-up" samples concurrently with the "required" sample for such metals. Further, EPA expects that enforcement officials will consider whether the owner/operator has taken such precautions to minimize the time during which they may be operating under violation conditions (if the dust concentration actually exceeds the "violation" limit) in determining appropriate enforcement action.

Except for "noncritical" metals where 30 continuous days of analyses demonstrate that the dust concentration for the metal does not exceed 10% of the concentration limit. For these metals, weekly composite samples must be analyzed. If a weekly composite exceeds 10% of the dust concentration limit, however, daily analyses would be again required.

The methodology requires that two dust concentration limits be established for each metal: a "conservative" limit and a "violation" limit. For example, the conservative limit is based on the safe enrichment factor of twice the enrichment factor at the upper 95% confidence level, while the violation limit is based on the enrichment factor at the upper 95% confidence level. If the conservative limit is failed more than 3 times out of 60 times, the owner/operator must notify the Director and he may burn hazardous waste for a total of 720 hours during which: (1) the series of 10 emissions tests must be conducted to revise the enrichment factor and the dust concentration limits; and (2) the maximum feed rate of each metal in the hazardous waste is reduced by 50% (except during the three compliance tests). If the violation limit is exceeded, however, the operator is in violation of the metals controls (and he must also notify the Director, reduce the feed rate of metals in hazardous waste, and conduct the series of 10 tests to calculate the revised concentration limits).

Notwithstanding these potential limitations, EPA believes that this methodology is preferable to the material balance approach. Rather than attempt to limit emissions by limiting metal feed rates and extrapolating through a number of not well-understood processes for furnaces that recycle dust, the methodology in the final rule goes to the material that is closest to what is being emitted, collected PM, to extrapolate to emissions.

Limits on the operating parameters discussed above will be established under this methodology during a minimum of three "compliance tests" of the first five of the ten emissions tests required to establish the enrichment factor for each metal. Consequently, during three of the ten runs, feed rates of metals in total hazardous waste and pumpable hazardous waste will be at the maximum level that the facility may operate during the remainder of interim status. Although the feed rate of metals in the hazardous waste during the other tests need not be at the maximum level established during the three "compliance tests", the feed rate must be at least 25%65 of the compliance test level, and the facility must operate at the compliance test capacity (i.e., the maximum capacity at which the facility may operate during the remainder of interim status). The owner and operator must demonstrate compliance with the applicable PM standard and the metals emissions standards of §266.106(c) or (d) during all ten tests required to establish enrichment factors. The rule requires that the ten emissions tests to determine enrichment factors be conducted in a two week period with not more than two tests per day, and that the three compliance tests (when metals feed rates from the hazardous waste will be maximized to establish limits for the remainder of interim status) be among the first five tests. EPA is providing these restrictions to ensure that the enrichment factors are representative of operations over several days when operating conditions can vary, and to ensure that any effect on enrichment factors from the high metals loading from spiked hazardous waste during the three compliance tests will be detected during the subsequent tests.

The testing and operating requirements for this methodology are prescribed in detail in "Alternative Methodology for Implementing Metals Controls" in the Methods Manual.

We are not requiring the facility operate at the maximum (i.e., compliance test) metals feed rate from hazardous waste (or other feedstreams) during all ten emissions tests because the purpose of the remaining tests is to obtain data to statistically determine the enrichment factor. Thus, it is important to determine how the enrichment factor may change as the feed rate of metals from various feedstreams varies. Nonetheless, the metal feed rate in the hazardous waste must me a minimum of 25% of compliance test limits during the remaining 7 enrichment factor determination tests.

b. Daily Emissions Testing. Under this option, the owner or operator must conduct daily emissions testing to confirm that the metals emissions limits are not exceeded. Sampling must be conducted for a minimum of 6 hours each day when hazardous waste is burned. To ensure that sampled emissions are representative of normal emissions that day, the testing must be conducted when burning normal hazardous waste for that day (i.e., considering metals content, point of introduction into the system, and physical form of the waste) at normal feed rates for that day and when the air pollution control system is operated under normal conditions. See §266.103(c)(3)(ii)(B).

Given that actual emissions sampling is used under this option to determine compliance with emission standards, those operating conditions that apply to other BIFs after certification of compliance that are designed to control metals emissions are not necessary. See §266.103(c)(1). The operating parameters that need <u>not</u> be limited at certification of compliance under this method are:

- Maximum feed rate of each metal in total feedstreams, total hazardous waste feedstreams, or pumpable hazardous waste feedstreams;
- Maximum feed rate of pumpable hazardous waste;
- Maximum feed rate of chlorine in total feedstreams;
- Maximum combustion chamber temperature and temperature at the inlet to the air pollution control system (APCS); and
- Key parameters to ensure proper operation of the APCS.

This approach has one drawback -- there is a time delay before a violation of the emissions limits is determined given that it normally takes a week or more to obtain the results of the stack sampling. To minimize the impact of this problem, the operator is required to know the metals concentration and feed rate of hazardous waste at all times and must determine if a change in metal feed rate from the hazardous waste is likely to result in exceedance of a metal emission limit.

c. Conditioning Prior to Compliance Testing. Under this approach (see §266.103(c)(3)(ii)(C)), the operator must condition the furnace to ensure that metals emissions are in equilibrium with metals fed into the system from all feedstreams. The owner or operator must determine using engineering judgment when the system has

reached equilibrium (i.e., how long the system must be conditioned). During conditioning, hazardous waste and raw materials having the same metals content as will be fed during the compliance test must be fed at feed rates that will be fed during the compliance test.

Under this method, limits for all operating parameters under §266.103(c)(1) must be established during the compliance test.

5. Trial Burns. A trial burn, or data in lieu of the trial burn (e.g., emissions data from interim status compliance testing) is required to demonstrate the performance capabilities of a system and to establish the operating limits of a facility for the duration of the operating permit. Compliance limits will be based on the operating conditions and emission rates observed during the trial burn. Therefore, to obtain the most flexible compliance limits, an owner/operator should conduct test burns and the trial burn under worst-case conditions (those that maximize emissions without exceeding the established limits). These conditions include feeding the waste used in the trial burn at a feed rate and metals concentration that reflect the highest levels expected in present or future operations.

Spiking with Metals. To achieve the maximum allowable concentrations of metals, the owner/operator may wish to spike the waste to artificially high concentrations of the metals during the pre-trial burn period and during the trial burn. However, the owner/operator may not feed metals at levels higher than those documented in the Part B permit application as those not likely to result in emissions exceeding allowable levels. Permit officials will consider this documentation in establishing pre-trial burn permit conditions for new permits.

### 6. Monitoring and Analysis Requirements.

a. Emissions Testing. Emissions testing and analysis for metals must be conducted using "Methodology for the Determination of Metal Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes" provided in Methods Manual for Compliance with the BIF Regulations<sup>66</sup>, incorporated by reference in §260.11. The methodology describes the use of a multiple metals sampling train. The methodology also describes and provides references to the appropriate analytical techniques in Test Methods for Evaluation Solid Wastes (SW-846), incorporated by reference in §260.11, that must be used to analyze samples.

U.S. EPA, Methods Manual for Compliance with the BIF Regulations, December 1990, EPA/530-SW-91-010. NTIS publication number PB91-120-006.

b. Analysis of Feedstreams. Feedstreams must be analyzed for each of the 10 regulated metals that could reasonably be expected to be in the hazardous waste. If a particular metal is excluded from the analysis, the basis for exclusion must be documented and included in the operating record. Methods for sampling and analysis of feedstreams for metals are prescribed in SW-846.

#### D. Interim Status Compliance Requirements

As prescribed in §266.103, and discussed in section VII of Part Three of this preamble, boilers and industrial furnaces operating under interim status must comply with the metals emissions standards during interim status.

### V. Controls for Emissions of Hydrogen Chloride and Chlorine Gas

Today's final rule uses a three-tiered regulatory approach to limit HCl and Cl<sub>2</sub> emissions (see §266.107), an approach identical to that used to control noncarcinogenic toxic metals emissions.

#### A. Background Information

In the 1987 proposed rule, EPA stated its intention to develop risk-based HCl emission standards in the same format and for the same reasons as the proposed metals emission limits. The HCl emission limits for a particular device would have been based on the device type and capacity, and on the type of surrounding terrain. In the 1989 supplemental notice, EPA discussed an alternative approach to make the standards a function of stack height, terrain, and land use rather than a function of device type and capacity. The reasons for the change were the same as those described above in the discussion of the metals standards.

Controls on Cl<sub>2</sub> were proposed on April 27, 1990 (55 FR 17866) because Cl<sub>2</sub> can be emitted from devices burning chlorinated wastes if insufficient hydrogen is available (i.e., from other hydrocarbon compounds or water vapor) to react with all of the chlorine present in the waste. In recent tests<sup>67</sup> of a cement kiln, EPA found that approximately 50% of gaseous chlorine emissions were in the form of Cl<sub>2</sub> (and the other 50% was in the form of HCl). In the April 1990 proposal, the Agency proposed a Cl<sub>2</sub> RAC of 0.4 ug/m<sup>3</sup>.

U.S. EPA, Emission Testing of a Precalciner Cement Kiln at Louisville, Nebraska, November 1990. Document No. EPA/530-SW-91-016.

In the 1989 supplemental notice, EPA also discussed the possibility of using continuous HCl monitors in lieu of the waste feed analysis approach for monitoring HCl emissions when emissions are likely to be close to allowable emissions. The Agency continues to believe that this is a reasonable approach and believes that it can be effectively implemented during the permit process as necessary using the omnibus authority.<sup>68</sup>

#### B. Response to Comments

The Agency received a number of comments on the proposed HCl and Cl<sub>2</sub> controls as discussed below.

1. Short-Term HCl RAC. A number of commenters stated that the Agency's support for the proposed 3-minute RAC for HCl was inadequate. The Agency is currently developing a new methodology for evaluating health effects data to develop a no-adverse-effect short-term exposure level.<sup>69</sup> Given that the new methodology has not been approved by the Agency, today's final rule does not establish a short-term RAC for HCl.

We note that the Tier I chlorine feed rate limits proposed in the 1989 supplemental notice were based on the short-term HCl RAC because the short-term exposure RAC provided more restrictive feed rate limits than the long-term RAC. Consequently, the 1989 proposed chlorine feed rate limits are not included in today's final rule. In establishing the Tier I feed rate limits for chlorine in today's final rule, the Agency considered both the long-term HCl RAC (i.e., 7 ug/m³) and the Cl<sub>2</sub> RAC (i.e., 0.4 ug/m³), and the partitioning between the two pollutants in stack gases. Given that the Agency has tested for Cl<sub>2</sub> emissions at only two facilities, and at one of the facilities more than 50% of the chlorine partitioned to Cl<sub>2</sub>, the Agency conservatively assumed in calculating feed rate limits that 100% of the chlorine would be partitioned to Cl<sub>2</sub>. Because the Cl<sub>2</sub> RAC is more than an order of magnitude lower than the HCl RAC, the Tier I chlorine limits were based on 100% conversion of chlorine to Cl<sub>2</sub>. If applicants believe that this assumption is too conservative, they may conduct emissions testing to document Cl<sub>2</sub> and HCl emission rates.

EPA notes that permit writers choosing to invoke the omnibus permit authority of §270.32(b)(2) to add conditions to a RCRA permit must show that such conditions are necessary to ensure protection of human health and the environment and must provide support for the conditions to interested parties and accept and respond to comment. In addition, permit writers must justify in the administrative record supporting the permit any decisions based on omnibus authority.

Memorandum dated September 18 from Susan Griffin, EPA, to Bob Holloway, EPA, entitled "Derivation of Short-Term RAC for HCl".

2. Need for Cl<sub>2</sub> Controls. Many commenters stated that Cl<sub>2</sub> controls are unnecessary. One commenter believed that very little hydrogen is needed to react with Cl<sub>2</sub> to form HCl. Another commenter believed that operating conditions for boilers and industrial furnaces are not conducive to the formation of Cl<sub>2</sub>. Another commenter stated that the proposed limits to control HCl emissions will provide adequate control of Cl<sub>2</sub> emissions as well.

The Agency does not agree with these commenters. As discussed above, emissions testing indicates that a substantial fraction of gaseous chlorine can be emitted in the form of Cl<sub>2</sub>. In addition, the HCl controls may not be adequate to control Cl<sub>2</sub> emissions. Because Cl<sub>2</sub> has a much lower solubility in water than does HCl, the use of wet scrubbers as the principle emissions control device for HCl is not likely to significantly reduce emissions of Cl<sub>2</sub>. Cl<sub>2</sub> emissions can be controlled, however, by increasing the hydrogen content of feed streams (e.g., by adding steam) or by decreasing the feed rate of chlorine. Moreover, EPA does not believe that high Cl<sub>2</sub> emissions relative to HCl emissions is a widespread occurrence.

3. HCl Emission Test Procedures. A number of commenters who own or operate cement kilns expressed concern that EPA's HCl stack sampling and analysis procedure (see section 3.3 in Methods Manual for Compliance with the BIF Regulations) was inappropriate because it counted as HCl chlorine in inorganic chloride salts and chloride ions that are emitted as ammonium chloride. The Agency has determined<sup>70</sup> that the filter in the sample probe, in fact, effectively removes fine particulate chloride salts so that they do not interfere with the HCl determination. The Agency agrees, however, with commenters that the procedure may consider as HCl chloride ions that are emitted as ammonium chloride.<sup>71</sup> Although the Agency has not developed a sampling and analysis procedure that would correct this problem, we do not believe that any such over-reporting of HCl will cause a cement kiln to exceed the HCl standard. This is because the highly alkaline particulate matter resulting from the limestone raw materials effectively neutralizes much of the chlorine generated from hazardous waste fed into the kiln.

<sup>70</sup> U.S. EPA, Emission Testing of a Precalciner Cement Kiln at Louisville, Nebraska, November 1990. Document No. EPA/530-SW-91-016.

U.S. EPA, Emissions Testing of a Wet Cement Kiln at Hannibal. MO, December 1990. Document No. EPA/530-SW-91-017.

4. Technology-Based HCl Controls. Several commenters stated that technology-based HCl emission controls applicable to hazardous waste incinerators (i.e., 99% reduction of emissions in the stack gas) should also apply to BIFs. As discussed in the proposed rule, the Agency continues to believe that a 99% reduction standard for BIFs to control HCl emissions may be neither technically feasible nor necessary to protect human health and the environment. The Agency believes that the process chemistry of some industrial furnaces (e.g., cement kilns) generally results in low HCl emissions and concerns about tube corrosion generally limit HCl concentrations in boiler emissions. Given the low uncontrolled HCl concentrations in many BIFs, a 99% reduction standard in addition to the health-based standard required by today's final rule, may not be cost-effective. Commenters did not provide data or information that would support the need for, and the cost-effectiveness of a technology-based standard in addition to the health-based standard provided by the final rule.

We note that the Agency is currently developing health effects data for two other acid gases: hydrogen fluoride and hydrogen bromide.

### C. Implementation

Procedures for implementing the HCl and Cl<sub>2</sub> controls are virtually identical to those for the metals controls discussed above.

- 1. Emissions Testing. Collection and analysis of HCl and Cl<sub>2</sub> in stack gas emission samples must be conducted according to the procedures prescribed in section 3.3 of the Methods Manual for Compliance with the BIF Regulations, (Methods Manual) incorporated by reference in §260.11. The Methods Manual describes two procedures for sampling emissions for HCl and Cl<sub>2</sub>: Methods 0050 and 0051. Method 0050 collects a sample isokinetically and is, therefore, particularly suited for sampling at sources emitting acid particulate matter (e.g., HCl dissolved in water droplets), such as those controlled by wet scrubbers. Method 0051 uses a midget impinger train sampling method designed for sampling sources of HCl and Cl<sub>2</sub> emissions not in particulate form. Samples collected using either method must be analyzed using Method 9057 which is also described in the Methods Manual.
- 2. Wastes Analysis. Methods for sampling and analysis of feedstreams for total chlorine and chloride are described in detail in SW-846.

3. Interim Status Compliance Requirements. As discussed in section VII of Part Three of this preamble, boilers and industrial furnaces operating under interim status must comply with the HCl and Cl<sub>2</sub> emissions standards during interim status.

## VI. Nontechnical Requirements

As proposed, the final rule requires BIFs to comply with the nontechnical standards applicable to other hazardous waste treatment, storage, and disposal facilities. These nontechnical standards address the potential hazards from spills, fires, explosions, and unintended egress; require compliance with the manifest system to complete the cradle to grave tracking system; ensure that hazardous wastes (and hazardous residues) are removed from the site upon closure; and ensure that the owners and operators are financially capable of complying with the standards. BIFs burning hazardous waste fuels that operate storage facilities must already comply with these standards under existing §266.35(c).

We also note, in particular, that owners and operators of BIFs are subject to the waste analysis requirements of §§264.13 and 265.13 by reference. See §§266.102(a)(2)(ii) for permitted facilities, and 266.103(a)(4)(ii) for interim status facilities. Before a waste is stored or burned, the owner or operator must obtain a detailed chemical and physical analysis of a representative sample of the waste sufficient to enable the owner or operator to comply with today's rule.

The nontechnical standards provided in today's rule are identical to those that currently apply to hazardous waste incinerators. In today's rule, \$266.102(a)(2) applies these standards to permitted BIFs and \$266.103(a)(4) applies these standards to BIFs operating in interim status.

Finally, we note that, as proposed, today's rule applies the same controls on fugitive emissions that currently apply to hazardous waste incinerators. The controls apply to facilities operating under a permit (see §266.102(7)(i)) and, on the effective date of the rule, to facilities operating under interim status (see §266.103(h)). The controls provide for alternative control strategies including: (1) keeping the combustion zone where hazardous waste is burned (or where emissions from such burning may migrate) totally sealed; and (2) maintaining the combustion zone pressure lower than atmospheric pressure.

#### VII. Interim Status Standards

In addition to the nontechnical standards discussed above, today's final rule requires facilities with interim status to comply with substantive emissions controls for metals, HCl, Cl<sub>2</sub>, particulates, and CO (and, where applicable, HC and dioxins and furans). Owners and operators must certify compliance with the emissions controls under a prescribed schedule, establish limits on prescribed operating parameters, and operate within those limits throughout interim status.

Given that interim status requirements are self-implementing, the Agency has developed comprehensive interim status requirements to ensure that the standards are implemented effectively. To assist the regulated community in complying with the requirements, EPA is developing a guidance document entitled Interim Status Guidance Document for BIFs (ISGD). The guidance document will be available shortly after publication of the final rule in the Federal Register. The ISGD will summarize the provisions of the rule, provide example forms that may be used to submit data and information required by the certifications of precompliance and compliance (see discussions below), and provide guidance on developing a compliance test protocol. To provide further assistance to the regulated community, EPA plans to conduct a series of workshops open to the public to explain how the interim status standards work. The workshops are scheduled to begin shortly after publication of the final rule in the Federal Register. To obtain a copy of the ISGD or information on the dates and locations of the workshop, contact the sources identified at the beginning of this preamble under "FOR FURTHER INFORMATION CONTACT".

The following sections summarize how the interim status standards work.

# A. Certification Schedule.

1. Certification of Precompliance. The BIF rule is effective 6 months after the date of promulgation. By the effective date, an owner/operator must submit a certification of precompliance providing prescribed information supporting a determination that emissions of individual metals, HCl, Cl<sub>2</sub>, and particulates are not likely to exceed allowable levels. See §266.103(b)(2). For certification of precompliance, the owner/operator must use engineering judgment to evaluate available information and data (or must use EPA-prescribed default data provided in sections 8.0 and 9.0 of Methods Manual for Compliance with the BIF Regulations, incorporated by reference in §266.11) to determine

that, under the operating limits (for EPA-prescribed parameters) that the owner/operator establishes, emissions are not likely to exceed the allowable emissions provided by §§266.105, 266.106, and 266.107. The owner and operator must then comply with these operating conditions (see discussion in section VII.B below) submitted in the precompliance certification during the interim status period of operation until a revised precompliance certification is submitted or until a certification of compliance is submitted as discussed below.

In addition, by the effective date of the rule, the owner or operator must submit a notice for publication in a major local newspaper of general circulation providing the general facility information prescribed by §266.103(b)(5). The information that must be provided in the notice includes: the name and address of the owner and operator of the facility; the type of facility, the type and quantity of hazardous waste burned; the location where the operating record of the facility can be viewed; a notification that a facility mailing list is being established so that interested parties may notify the Agency that they wish to be placed on the mailing list to receive future information and notices about the facility; a brief summary of the RCRA regulatory system for BIFs; and the address of the EPA Regional Office where additional information on the RCRA regulatory system may be obtained. EPA is requiring this public notice to ensure that the local citizenry is aware that the BIF is burning hazardous waste and that, to the extent desired, the local citizenry may become better informed about the facility operations through site inspections and review of data in the operating record. In turn, this opportunity for local involvement in facility operations should provide an added incentive for the owner and operator to comply with the spirit and letter of the interim status standards.

EPA notes that facilities that meet the definition of "in existence" of §266.103(a)(1)(ii) but that are not burning hazardous waste on the effective date of the rule must nonetheless submit a certification of precompliance based on planned operations. The certification may be revised at any time in the future if necessary. See §266.103(b)(8).

2. Certification of Compliance. Within 18 months of promulgation, the owner/operator must conduct compliance testing<sup>72</sup> and submit a certification of compliance

We note that compliance testing may be conducted only under operating conditions for which the facility has submitted a certification of precompliance. This is because the facility may only operate after the effective date of the rule and prior to submittal of a certification of compliance under conditions for which it has certified precompliance. If any applicable emission standard is exceeded during the compliance test (or during

with the standards for individual metals (§266.106), HCl and Cl<sub>2</sub> (§266.107), particulates (§266.105), and CO, and, where applicable, HC and dioxins/furans (§266.104(b) through e)). The certification of compliance is based on emissions testing and establishes operating limits for EPA-prescribed parameters based on the compliance test. See §266.103(c)(1).

If the owner/operator cannot submit the certification of compliance within 18 months of promulgation, however, he must either: (1) notify the Director that he is taking an automatic 12-month extension under which hazardous waste burning is limited to a total of 720 hours; (2) obtain a case-by-case extension of time for reasons beyond his control; or (3) stop burning hazardous waste and begin closure of the hazardous waste portion of the facility. See §266.103(c)(6).

The case-by-case time extension will be provided by the Director if he determines that the owner or operator has made a good faith effort to comply with the requirements in a timely manner but, for reasons beyond his/her control, are not able to meet the certification of compliance deadline. Reasons could include inability to complete modifications to an air pollution control system in time to conduct the compliance test to support the certification, or a major, unplanned outage of the facility (e.g., need to replace refractory in a kiln) just prior to scheduled compliance testing, or as discussed earlier, HC levels attributable to organics in raw materials. The Director may use his discretion to determine the length of the extension.<sup>73</sup> The Director also may impose conditions that ensure that the boiler or industrial furnace will be operated in a manner that protects human health and the environment, provided that the Director documents the basis for adding such a condition and provides the applicant opportunity to comment on it.

In addition, we note that a case-by-case extension may be requested and granted for any interim status certification deadline. A case-by-case extension may be granted after an owner/operator has elected to take the 12-month automatic extension, an extension may be granted if the owner/operator cannot comply with the recertification schedule (see discussion below), and an existing extension may be extended.

pretesting), the facility must immediately submit a revised certification of precompliance establishing revised (i.e., more stringent) operating limits.

We would not expect for the Director normally to limit the hours that hazardous waste may be burned under a case-by-case extension given that the owner/operator must support the need for the extension and, if granted, the extension must be for a legitimate need. In contrast, the hours of burning are limited for the automatic 12-month extension because there is no judgement by the Director that, in fact, the extension is warranted.

- 3. Recertification. Owners and operators must periodically conduct compliance testing and recertify compliance with the standards for individual metals, HCl and Cl<sub>2</sub>, particulates, and CO, and, where applicable, HC and dioxins/furans within three years of the previous certification while they remain in interim status (i.e., until an operating permit is issued under §270.66). See §266.103(d). EPA is requiring recertifications primarily to ensure that air pollution control systems do not deteriorate over time.
- 4. Failure to Comply with the Certification Schedule. If the owner or operator does not comply withe the certification schedule, all hazardous waste burning must cease as of the date of the missed deadline, and closure must commence. See §266.103(e). Any burning of hazardous waste by such a device after failure to comply with the certification schedule must be under a RCRA operating permit. See §270.66.

To comply with the certification schedule, complete and accurate certifications of precompliance and compliance must be submitted by the applicable deadlines. (Although the deadline for certification of compliance may be extended (see §266.103(c)(7)), the deadline for certification of precompliance may not be extended.) In addition to terminating interim status if the owner and operator do not comply with the certification schedule, EPA will also take appropriate enforcement action.

When closing a BIF, all hazardous waste and hazardous waste residues, including, but not limited to, ash, scrubber water, and scrubber sludges, must be removed from the affected BIF. In addition, the owner/operator must comply with the general interim status closure requirements of §§265.111-265.115, as amended. These requirements, which are incorporated by reference into today's rule, specify closure performance standards; submission of and compliance with a written closure plan; disposal or decontamination of equipment, structures, and soils; and certification procedures for closure.

We note that under amended §265.112(d)(2), for an owner or operator who fails to submit a complete certification of compliance by the applicable compliance deadline (including the automatic 12-month extension or the case-by-case extension under §266.103(c)(6)(i)(B)), the date that he "expects to begin closure" is within 30 days after the applicable deadline. Therefore, for example, for an owner who takes the automatic 12-month extension, the closure notification requirements of §265.112(d)(1) or the closure activity requirements of §265.113 would not be triggered unless and until the owner fails to

submit a complete certification of compliance by the 12-month extended deadline and a case-by-case extension beyond the 12-month extension was not obtained.

For any other BIF owner or operator closing during interim status operation (i.e., one who closes between the effective date of the rule but before the interim status compliance deadline of 18 months after promulgation of the rule, or one who submits a complete certification of compliance by the applicable 18-month compliance deadline, the 12-month automatic extension, or case-by-case extension, and closes during interim status), the date when he "expects to begin closure" under 265.112(d)(2) will remain either within 30 days after the date on which any hazardous waste management unit receives the known final volume of hazardous waste, or if there is a reasonable possibility that the unit will receive additional hazardous waste, no later than one year after the date on which the unit received the most recent volume of hazardous waste.

5. Development of the Certification Schedule. In the 1989 supplemental notice, the Agency requested comment on alternative schedules for requiring compliance with the emissions standards during interim status. The Agency selected a certification deadline of 18 months (with provision for extensions) because we believe that most facilities will be able to install the necessary monitoring equipment, conduct any precompliance testing that may be necessary, and conduct compliance testing within that time period. Although 18 months from the date of promulgation is a fairly short period of time, we note that Agency staff have made numerous public presentations and have had numerous discussions<sup>74</sup> with the regulated community, including, in particular, the development of interim status compliance procedures. Thus, facility owners/operators have had some advance indication of the general regulatory approach taken in the final rule.

The Agency received a comment that the air emission standards for cement kilns should be instituted more quickly than the schedule proposed. The commenter believed that accelerating the schedule will not place an excessive burden on these facilities because the regulations were proposed far enough in advance for cement kilns to come into compliance. The Agency has considered this comment and: (1) sees no compelling reason to single out cement kilns from other BIFs for an accelerated schedule; and (2) continues to believe that an 18-month compliance period is representative of the time required to

See the public docket for this rulemaking for summaries of meetings held with groups including: Cement Kiln Recycling Coalition, Chemical Manufacturers Association, National Solid Waste Management Association, Council of Industrial Boiler Operators, and Hazardous Waste Treatment Council.

implement necessary plant design or process modifications, install monitoring and compliance equipment, conduct facility compliance testing, and submit a certification of compliance testing that documents key operating limits during the remainder of the interim status period. In fact, the Agency is concerned that in some situations, where, for example, the air pollution control system may need to be modified, an 18-month deadline may not provide enough time to complete modifications, "shake-down" the system, conduct pre-testing<sup>75</sup>, conduct compliance testing, and analyze test data and submit a certification of compliance. Thus, the final rule includes provisions for time extensions to all certification deadlines.

### B. Limits on Operating Parameters

Limits on operating parameters during interim status are established at certification of precompliance and at certification of compliance following emissions testing 18 months (unless extended) after promulgation of the rule. The operating conditions can be revised prior to certification of compliance by submitting a revised certification of precompliance. The operating conditions can be revised after certification of compliance by conducting emissions testing and submitting a revised certification of compliance.

After the effective date of the rule and prior to certification of compliance with the emissions standards based on emissions testing, a facility may operate only under those conditions for which the facility has submitted a "precompliance" certification demonstrating that emissions of individual metals, HCl, Cl<sub>2</sub>, and particulates are not likely to exceed allowable levels. The operating conditions for which limits are established by precompliance are (see §266.103(b)(3)):

- Feed rate of each of the 10 metals in:
- Total feed streams, except for furnaces that recycle collected particulate matter (see discussion in section VII.I below)
  - Total hazardous waste feed streams
  - Total pumpable hazardous waste feed streams;
  - Total feed rate of chlorine in all feed streams;
  - Total feed rate of ash in all feed streams, except for cement and light-weight aggregate facilities for which ash content of feed streams is not an operating parameter;

Although pretesting is not required, EPA believes that most facilities will conduct pretesting before conducting the formal compliance testing with all its attendant QA/QC requirements.

- Total feed rate of hazardous waste and feed rate of pumpable hazardous waste; and
- Maximum capacity in appropriate units such as heat input, steam production, or raw material feed rate.

In addition, the following parameters must be considered in demonstrating precompliance and must be continuously monitored (and records maintained in the operating log) when monitoring systems are installed (see §266.103(b)(6)):

- Maximum combustion zone temperature;
- Maximum flue gas temperature entering the PM APCS; and
- Limits for APCS-specific operating parameters.

Once a facility has conducted compliance testing and certified compliance with the emissions standards, limits for all of the above parameters, as well as for CO (and, where applicable, HC) are established based on the compliance test and remain in force until recertification under new conditions. See §266.103(c)(1).

# C. Automatic Waste Feed Cutoff

Upon certification of compliance, an automatic hazardous waste feed cutoff system must engage when the limits (established in the certification) for the following operating parameters are exceeded (see §266.103(h)):

- Total feed rate of hazardous waste and feed rate of pumpable hazardous waste;
- Limits on CO and, where applicable, HC;
- Maximum capacity in appropriate units such as heat input, steam production, or raw material feed rate;
- Maximum combustion zone temperature;
- Maximum flue gas temperature entering the PM APCS; and
- Limits for APCS-specific operating parameters.

Facilities operating during interim status after certification of compliance must test the automatic waste feed shutoff system once every 7 days to ensure that it is operating properly, unless an owner/operator can document that weekly testing will result in unsafe conditions. See §266.103(k)(iii). In all cases, testing at least every 30 days is required.

Owners/operators are required to document the results of these tests and all automatic waste feed shutoffs that occur during normal operations.

#### D. Sham Recycling Policy

The BIF rules supersede the Agency's sham recycling policy (see 48 FR 11157 (March 16, 1983)) after the owner or operator certifies during interim status compliance with the emissions standards for metals, HCl, Cl<sub>2</sub>, particulates, and CO (and, where applicable, HC and dioxins and furans). Thus, after certification of compliance, a BIF may burn hazardous waste (other than waste fed solely as an ingredient or solely for material recovery) with a heating value lower than the 5,000 Btu/lb limit generally considered heretofore to be the minimum for a legitimate hazardous waste fuel. Although the Agency considers such burning to be treatment, we believe that conformance with the emissions standards upon certification of compliance under §266.103(c) will ensure protection of human health and the environment. (Prior to today's rule, BIFs burning a hazardous waste that was not considered to be a legitimate fuel were subject to the Subpart O incinerator standards of Parts 264 and 265, assuming burning was not for some other legitimate recycling purpose, such as material recovery.)

Although we indicated above that a BIF may burn hazardous waste for the purpose of treatment upon certification of compliance, today's rule allows BIFs to burn such hazardous waste for a total period of time not to exceed 720 hours prior to certification of compliance. See \$266.103(a)(6). The rule allows such burning only for purposes of compliance testing (and pretesting to prepare for compliance testing) to determine that the device can comply with the emissions standards while burning waste for treatment. The rule limits such burning to a total of 720 hours because we believe that period of time is adequate to complete any pretesting and compliance testing, and it is the same period of time that new BIFs may burn hazardous waste during the pretrial burn period under \$270.66(b)(1).

The Agency discussed three options in the 1989 supplemental notice for superseding the sham recycling policy: rescinding the sham recycling policy on the effective date of the final rule; rescinding the sham recycling policy when a facility comes into compliance with the interim status emission standards; or leaving the sham recycling policy in effect until a RCRA operating permit is issued.

The Agency received comments supporting all three of the options. Eight commenters supported the first option, rescinding the sham recycling policy on the effective date of the final rule, because the policy is considered guidance. Eight commenters supported the second option, rescinding the sham recycling policy when facilities come into compliance with the interim status emission standards, because the standards are protective of human health and the environment. Five commenters supported the third option, leaving the sham recycling policy in effect until a facility is issued a RCRA operating permit, because the permit writer oversight during the permit process is necessary to ensure that a facility complies with the appropriate regulations.

The Agency believes that the procedures required for certification of the interim status emissions standards are adequate to ensure effective implementation and enforcement of the standards. The only emissions standard applicable to permitted facilities that is not required during interim status is the destruction and removal efficiency (DRE) standard requiring a trial burn to demonstrate 99.99% DRE. The Agency does not believe that this is necessary because emissions testing of boilers and industrial furnaces indicates that facilities with CO and HC levels within the limits established by today's rule also are likely to achieve 99.99% DRE.

It should be noted that in rescinding the sham recycling policy for these types of regulated boilers and industrial furnaces, the Agency is not altering in any way what secondary materials are defined as solid and hazardous wastes when burned for legitimate energy recovery. Thus, all spent materials, sludges, and by-products are solid wastes when burned for recovery, as are off-specification commercial chemical products which are burned as fuels (or used as a component of fuels) in lieu of their original intended use. See §§261.2(c)(2) and 261.33. (Non-listed hazardous commercial chemical products (i.e., those that exhibit a characteristic but are not listed in §261.33) are likewise solid wastes when they are recycled in ways that differ from their normal use. 50 FR at 14219 (April 11, 1985).) With respect to the issue of what constitutes a normal manner of use for an off-specification commercial chemical product that has some Btu value, or the issue of when such a material is used "in lieu of [its] original intended use" (§261.33) and so is a solid and hazardous waste, the Agency notes that not every type of burning ostensibly for energy recovery is considered to qualify. Inappropriate modes of burning thus do not render such materials non-wastes. For example, if ignitable off-specification natural gas condensate is burned as a motor fuel, or reactive jet fuel (U 133, hydrazine) is burned as conventional fuel oil, such materials are solid and hazardous wastes and subject to subtitle

C controls. This is because the mode of burning is not at all like these materials' original intended use.

#### E. Submittal of Part B Applications

Permit writers will require owners and operators to submit Part B applications for operating permits on a schedule considering the relative hazard to human health and environment the facility poses compared to other storage, treatment, and disposal facilities within the Director's purview.

#### F. DRE Testing

As proposed, testing to demonstrate 99.99% destruction and removal efficiency (DRE) of organic compounds in the waste is not required under interim status. The complexity and costs of DRE testing, as well as the substantial interaction needed between owners/operators and regulatory officials, make such testing impracticable during interim status. EPA expects that the control requirements for CO and HC will result in low levels of emissions of organic compounds.

#### G. Chlorinated Dioxins and Furans

As proposed, hazardous waste containing or derived from any of the following dioxin-listed wastes cannot be burned in a boiler or industrial furnace operating under interim status: EPA Hazardous Waste Nos. F020, F021, F022, F023, F026, and F027. Burning these dioxin-containing wastes during interim status is prohibited because boilers and industrial furnaces cannot be assumed to achieve the 99.9999 percent DRE required for these wastes.

Even though these wastes may not be burned during interim status, chlorinated dioxins and furans may be emitted as PICs under certain conditions (i.e., when the PM control device is operated within the temperature range of 450-750°F, or when HC concentrations exceed 20 ppmv) as discussed in section II.E of Part Three of the preamble. EPA believes that the emissions testing and risk assessment requirements of \$266.104(e) can be effectively implemented during interim status without significant EPA interaction. Thus, the rule requires the owner or operator to certify compliance with those requirements, as applicable.

#### H. Special Requirements for Furnaces

Today's rule provides special interim status requirements industrial furnaces that feed hazardous waste, except hazardous waste fed solely as an ingredient<sup>76</sup>, at locations other than the "hot" end where the product is discharged and fuels are normally fired to ensure adequate combustion of hazardous waste prior to conducting a trial burn during the Part B permit process (see §266.103(a)(5)) as follows: (1) the combustion gases must have a minimum temperature of 1800°F at the point where the waste is introduced<sup>77</sup>; (2) the owner or operator must determine (and include such determination in the operating record) that there is sufficient oxygen present to combust the waste; (3) the continuous hydrocarbon monitoring controls provided by §266.104(d) apply; and (4) for cement kilns, hazardous waste must be fed into the kiln itself:

EPA established a minimum temperature of 1800°F for the location of hazardous waste firing and is requiring that the owner/operator demonstrate that adequate oxygen is present to sustain combustion given that it is generally accepted that organic compounds are readily destroyed at temperatures above 1800°F in the presence of adequate oxygen. The demonstration of adequate oxygen is particularly important for cement kilns because they are operated close to stoichiometric oxygen levels (i.e., with little excess oxygen in the kiln) to efficiently maintain the high temperatures necessary to calcine and sinter the raw materials. Although higher excess oxygen levels would better ensure more complete combustion of fuels, operating at higher oxygen levels is less thermally efficient and reduces the kiln production capacity.

Hazardous waste is burned solely as an ingredient if it is burned for neither energy recovery (i.e., it has a heating value less than 5,000 Btu/lb) nor treatment or destruction (i.e., it contains a total of less than 500 ppm toxic organic constituents listed in Appendix VIII, Part 261).

EPA is aware that cement companies have experimented with feeding containerized waste into the upper, raw material feed end of the kiln using feed chutes that propel the containers down into the kiln before they rupture and expose the waste to the combustion gas (and begin to release hydrocarbons). In such a situation, the temperature limit applies at the point that the waste may begin to release hydrocarbons — the point where the container impacts the charge bed. The temperature limit does not apply to the point where the container is actually charged into the kiln. (If, however, a noncontainerized waste is fired into the kiln at the upper end, the 1800°F temperature limit applies at the location where the waste exits the firing system.) Although this discussion pertains to cement kilns, EPA notes that the subject requirements apply to any industrial furnace that feeds hazardous waste at a location other than the "hot" end as described in the text.

In addition, continuous hydrocarbon (HC) monitoring is required to demonstrate that HC levels do not exceed the regulatory limit of 20 ppmv on a hourly rolling average basis (or alternative level established under §266.104(f)) irrespective of whether the CO level is less than 100 ppmv where HC monitoring is not normally required. See §266.103(a)(6). EPA is requiring HC monitoring because of the concern that CO monitoring alone may not be an adequate indicator of good combustion conditions when hazardous waste is fed at locations other than where (nonhazardous) fuels are normally fired. See discussion in Part Two, section II.A.4.a of this preamble. Continuous monitoring of HC and compliance with the applicable operating limit is required upon certification of compliance (or, for furnaces that feed raw materials containing organic matter and that receive a time extension to certify compliance, upon receipt of the time extension<sup>78</sup>).

The Agency considered whether the hydrocarbon controls were redundant to the operating requirements specified above and concluded that HC monitoring is needed to effectively implement and enforce the controls on organic emissions. Although the operating requirements alone should be adequate to limit organic emissions, absent HC monitoring there would be no continuous verification that the operating requirements were, in fact, adequate and that the owner/operator maintained compliance with the operating requirements.

Finally, the rule requires that hazardous waste be fired into a cement kiln itself to ensure that the waste is not introduced at a location that may not be conducive to complete combustion of the waste. For example, cement companies have considered burning hazardous waste in the precalciner of a cement kiln. Although such practices may prove during the permit process to be acceptable, EPA has not tested emissions from a kiln burning waste at locations other than in the kiln itself, and is concerned that complete combustion of organic constituents may not be ensured. Thus, burning hazardous waste in a cement kilns precalciner is not allowed during interim status. (This restriction is limited to cement kilns because this is the only type of kiln of which the Agency is aware where hazardous waste may be fired at a location that is clearly not designed for optimum combustion conditions. A cement kiln precalciner is designed primarily to achieve calcining of raw materials and may not provide adequate combustion of hazardous waste.)

We note, as discussed elsewhere in the text, the time extension will be conditional on, among other things, HC (and CO) levels not exceeding an interim limit established in the extension.

The special requirements do not apply to hazardous waste that is burned (processed) solely as an ingredient<sup>79</sup> because such waste does not contain significant levels of hazardous nonmetal constituents (i.e., compounds listed in Appendix VIII, Part 261) and, thus, nonmetal emissions will not pose significant risk to human health and the environment. (Metal emissions will be adequately controlled by today's rule irrespective if where the waste is fed into the system because metals are controlled by a PM control device.) Thus, emissions of nonmetal compounds are not of concern when a waste is burned (processed) solely as an ingredient. EPA considers a waste to be burned solely as an ingredient in a kiln if if is not burned partially as a fuel or for conventional treatment (i.e., destruction). The Agency considers a waste that is fed to boilers and industrial furnaces to be burned at least partially for energy recovery and not as an ingredient if it has a heating value of 5,000 Btu/lb or greater, as-generated, and at least partially for treatment (i.e., destruction) if it contains more than a total of 500 ppm (by weight) of Appendix VIII, Part 261, nonmetal hazardous constituents. See 54 FR at 43731-32 where EPA discussed use of a 500 ppm standard for distinguishing between recycling activities tantamount to production and those constituting conventional treatment.

The Agency notes in addition that it ordinarily does not consider metal-bearing wastes hazardous wastes to be used as ingredients when they are placed in industrial furnaces purportedly to contribute to producing a product. (The use of metal-bearing wastes for material recovery is discussed earlier in the preamble, and this discussion does not deal with the issue of when such wastes are burned for legitimate material recovery in industrial furnaces.) To be considered legitimate use as an ingredient, it would normally need to be demonstrated to EPA (or an authorized State) pursuant to §261.2(f) that the hazardous metal constituents in the waste are necessary for the product (i.e., are contributing to product quality) and are not present in amounts in excess of those necessary to contribute to product quality. See 50 FR at 638 (Jan. 4, 1985). This would normally require some demonstration that these hazardous metal constituents do not render the product unsafe for its intended use. (The other sham recycling criteria discussed frequently by EPA would also have to be satisfied. See, e.g., 53 FR at 522 (Jan. 8, 1988). The

Under the RCRA hazardous waste regulatory program, EPA considers a hazardous waste to be burned or processed as an ingredient if it is used to produce a product. EPA considers a hazardous waste to be burned or processed for material recovery if one or more constituents of the waste is recovered as a product. Nonetheless, the criteria are the same for determining when a waste is burned (or processed) as an ingredient or for materials recovery versus when it is burned for the partial purpose of energy recovery or conventional treatment.

types of uses of hazardous wastes in industrial furnaces to produce waste-derived products of which the Agency is aware, such as using hazardous wastes to produce aggregate or cement (the Agency is not actually aware of cement kilns using hazardous wastes ostensibly as ingredients, although some facilities have contemplated engaging in the practice) do not appear to satisfy these criteria. In addition, the Agency notes the discussion earlier in this preamble (in the context of hazardous waste used as slurry water) to the effect that the more common and less valuable the raw material the hazardous waste is replacing, the more likely the activity is to be some form of surrogate treatment.

# I. Special Metals Controls for Furnaces that Recycle Collected Particulate Matter

For reasons discussed in section V.B.4 of this preamble, the final rule requires owners and operators of furnaces (e.g., cement kilns, light-weight aggregate kilns with dry particulate matter (PM) control systems) that recycle collected PM back into the furnace to implement the metals emissions controls of \$266.106(c) or (d) under one of the three alternative methods. The discussion in section V.B.4 of the preamble summarizes procedures for certification of compliance under the methods. For certification of precompliance, the standard procedures will be used for both the "daily emissions testing" option, and the "conditioning prior to compliance testing" option. Precompliance procedures are different, however, for the "monitoring metals in collected PM" method, as discussed below.

Under the "monitoring metals in collected PM" method, operating limits will be established for the all of the parameters listed in section VII.B. above except for the feed rate limit on each metal in total feedstreams. In lieu of that parameter, the special procedures limit the concentration of each metal in collected PM. See "Alternative Methodology for Implementing Metals Controls" in Method Manual for Compliance with the BIF Regulations (incorporated by reference in §266.11).

For certification of precompliance, the owner/operator must estimate the enrichment factor for each metal using engineering judgment or EPA prescribed default values. EPA default values are 100 for mercury and 10 for all other metals. The enrichment factors are then used to calculate precompliance dust metal concentration limits using the allowable emission rate for each metal and the applicable PM standard using the same procedures applicable for certification of compliance. Daily (or weekly for noncritical metals) analysis of dust samples is required. If more than 3 of the previous 60 samples fail, the owner/operator must notify the Director. The owner/operator is then allowed to burn

hazardous waste for up to 720 hours before a revised certification of precompliance must be submitted that revises the estimated enrichment factors and establishes revised precompliance dust metals concentration limits. The revised enrichment factors must be based on testing or engineering judgment using data or information not considered in the original estimate.

# J. Recordkeeping

Over the period of interim status, facilities will be required to generate and maintain data and records designed to demonstrate routine compliance with established limits on operating parameters. These records must be sufficient to allow a RCRA inspector to review and evaluate recent and past operation of the facility for compliance purposes. Records must be maintained for a period of three years or until an operating permit is issued under §270.66, whichever is later.

# VIII. Implementation of Today's Rule

There are three types of treatment, storage, and disposal facilities (TSDF's) which may be affected by today's rule: (1) facilities which are subject to RCRA permit requirements for the first time as a result of today's rule; (2) facilities which are already operating under interim status; and (3) facilities that have been issued a RCRA permit. The following sections describe the compliance obligations for facilities that have units subject to permitting due to today's rule.

#### A. Newly Regulated Facilities

Prior to receiving a permit, newly regulated facilities (i.e., facilities which only contain the types of units newly regulated by today's final rule) must qualify for interim status by the effective date of the rule in order to continue managing hazardous wastes in units newly regulated by today's rule. To obtain interim status, the eligible facility must meet three criteria: (1) on the date of promulgation of the BIF rule, the facility must be "in existence" with respect to hazardous waste burning or processing activities; (2) within 90 days of the date of promulgation, the owner or operator must notify EPA or an authorized State (if not previously required to do so) of the facility's hazardous waste burning or processing activities; and (3) within 180 days of the date of promulgation, the owner or operator must submit Part A of the permit application.

- 1. Definition of "In Existence". To meet the definition of an existing facility, the boiler or industrial furnace must either be in operation burning or processing hazardous waste on or before the effective date of the rule, or construction of the facility (including the hazardous waste burning or processing equipment) must have commenced on or before the effective date of the rule. See §266.103(a)(1)(ii). A facility has commenced construction if the owner or operator has obtained the Federal, State, and local approvals or permits necessary to begin physical construction; and either:
  - (a) A continuous on-site, physical construction program has begun; or
  - (b) The owner or operator has entered into contractural obligations -- which cannot be cancelled or modified without substantial loss -- for physical construction of the facility to be completed within a reasonable time. See §270.2.
- 2. Section 3010 Notification. BIF owners and operators burning hazardous waste fuels have already been required to notify of their hazardous waste fuel activities under existing §266.35 and need not renotify. (See section 3010(a) which allows EPA to waive notification if the information is considered unnecessary.) Although today's rule requires small quantity burners and owners and operators of smelting, melting, and refining furnaces to notify, this notification is not a section 3010 notice and so is not a prerequisite to obtaining interim status.

Facilities which have not submitted a section 3010 notification form to EPA must do so by [insert date 90 days after publication in the FEDERAL REGISTER]. This is done by completing a section 3010 notification form and sending it to the appropriate EPA Regional Office. (See EPA form 8700-12, dated 7/90. See 55 FR 31389, August 2, 1990 for a copy of the form. Notification instructions are set forth in 45 FR 12746.)

3. Part A Permit Application. Newly regulated facilities must also submit a Part A permit application to the appropriate EPA Regional Office by [insert date 6 months after publication in the FEDERAL REGISTER], which is the effective date of today's rule. (See 270.70(a) and EPA Form 8700-23, dated 1/90.)

#### B. Interim Status Facilities

Interim status facilities that contain units newly regulated by today's rule must file an amended Part A permit application under 40 CFR 270.10(g) if they are to continue managing hazardous waste in these newly regulated units. The facilities must file the necessary amendments to EPA by [insert date 6 months after publication in the FEDERAL REGISTER], the effective date of the rule, or they will have to cease management of hazardous waste in these units. In authorized states, the facility should also send a copy of the submission to the State program.

Today's rule amends §270.72 to allow interim status facilities to add newly regulated units as a change in interim status without prior Agency approval. The current procedures for the addition of new units in §270.72(a)(3) require Agency approval prior to making the change. Section 270.72(a)(1) allows the addition of newly listed or identified wastes, and any newly regulated units associated with them, to be added to the Part A application without prior Agency approval. Today's addition of §270.72(a)(6) extends this ability to any newly regulated unit. Today's rule also eliminates the reconstruction limit for the addition of newly regulated types of units. (As noted earlier, the Agency proposed this specific change for boilers and industrial furnaces, but realized in the course of implementing the proposal that the problem was more endemic and called for a general solution.) This provision is located in §270.72(b)(7).

In order to add a unit as a change in interim status under the new §270.72(a)(6), the owner or operator must file the amended Part A permit application by the effective date of the rule that subjects the unit to regulation.

Technical Correction to \$270.73(f), (g). In the course of developing today's rule, the Agency discovered that particular regulatory provisions dealing with loss of interim status are miscodified. See \$\$270.73(f), (g). We are amending these provisions in today's notice to match the implementing statutory language. The result will be that neither boilers nor industrial furnaces, nor other units which achieve interim status after Nov. 7, 1984, are subject to the automatic statutory loss of interim status provisions.

The 1984 HSWA amendments provided that each facility which achieved interim status prior to the effective date of the amendments would automatically lose its interim status on a specified date, unless by an earlier specified date the facility applied for a final determination regarding the issuance of a permit (i.e., submitted Part B of its permit application). See RCRA sections 3005(c)(2), (e)92). The dates for Part B submission and loss of interim status vary according to whether the facility is a land disposal facility, incinerator, or other facility. Id. Of relevance to today's technical correction, HSWA provided that interim status for incinerators would terminate five years after the enactment

of HSWA (i.e., on November 8, 1989), unless the Part B application was submitted within two years after the enactment (i.e., by November 8, 1986); interim status for other non-land disposal facilities would terminate eight years after the HSWA amendments (i.e., November 8, 1992) unless the Part B application was submitted within four years (i.e., November 8, 1988). See RCRA section 3005(c)(2).

EPA amended its regulations on July 15, 1985 to incorporate these and other HSWA changes. See 50 FR at 28702. EPA's intention in promulgating these amendments was simply to reflect the new statutory provisions; for the most part, the Agency simply codified into the regulations the new HSWA language. Id. at 28703. In light of the largely ministerial nature of the regulations, and in view of the need to move quickly to incorporate HSWA, EPA published these 1985 regulations without opportunity for public comment. Id. (The D.C. Circuit eventually sustained the legality of these procedures in United Technologies Corp. v. EPA, 821 F. 2d at 714 (D.C. Circ.1987).)

Section 270.73(f), (g) sets forth the dates on which interim status for incinerators and other non-land disposal facilities terminates if the facilities fail to submit their Part B applications. However, in contrast to the HSWA amendments, the sections by their terms apply to all incinerator and other non-land disposal facilities, instead of being limited only to those facilities which had obtained interim status on November 8, 1984, the date of the HSWA amendments. In fact, it is impossible for units newly subject to regulation after the specified dates for submission of Part B permit applications (such as the boilers and furnaces regulated by today's rule, or certain facilities newly subject to regulation under the recent Toxicity Characteristic rule) to comply with the rules as codified. EPA did not intend for these rules to deviate from statutory language. As the preamble to the 1985 codification regulations stated, the Agency simply intended for section 270.73(f), (g) to reflect the HSWA termination-of-interim status provisions. Id. at 28723.

The Agency is today making a technical correction to these sections to correct this mistake, and to avoid the unintended (and possibly illegal) result that large classes of newly regulated units are ineligible for interim status because they failed to submit Part B applications at a time they were unregulated. EPA is proceeding without proposing the correction for public comment, and believes that public comment is unnecessary, for the following reasons: (1) this correction simply conforms the language of the regulations to the Agency's original expressed intent in promulgating the 1985 regulations, which themselves were validly promulgated without the opportunity for comment; (2) this correction simply conforms the regulations to HSWA's plain language; (3) the amendment

conforms the regulations to the Agency's actual practice in implementing the regulations and RCRA 3005(c)(2); (4) the amendment is necessary to avoid rendering units newly regulated after specified Part B permit application submittal dates from being ineligible for interim status even though they meet all of the statutory interim status eligibility criteria; and (5) the amendment can be viewed as an interpretative rule, which does not require prior notice and public comment.

#### C. Permitted Facilities

Some permitted facilities contain boiler and furnace units that are newly subject to Subtitle C regulation as a result of today's rule. These permitted facilities must therefore submit permit modifications to EPA Regional offices, and comply with federal permit modification procedures in order to continue to manage hazardous waste in these units. The modification will be processed under Federal permit modification procedures rather than authorized state procedures because this rule is promulgated under HSWA authority. However, because the permit undergoing modification is most likely a jointly issued EPA-state RCRA permit, a copy of the modification request should also be submitted to the state if it is an authorized state.

1. Amendment to §270.42(g). Today's rule contains a new permit modification procedure in §270.42 for the addition of any newly regulated waste management units used to manage hazardous wastes (see §270.42(g)). This two-step procedure essentially allows the permittee to notify the Agency of its newly regulated boilers and furnaces using the Class 1 permit modification procedures, and to continue to handle hazardous wastes. Subsequently, the permittee must submit a Class 2 or 3 permit modification request to initiate a permanent change to the permit. The self-implementing interim status standards of §266.103 would apply until the permit was modified using the Class 2 or 3 modification procedures. This new permit modification provision only applies to newly regulated units that were not previously subject to the permitting requirements of Subtitle C of RCRA.

Today's new permit modification provision for newly regulated units is essentially identical to the special procedure in §270.42(g) for newly regulated wastes. The purpose of today's amendment is to extend the same opportunities and procedures that are available for newly regulated waste streams (and any units used to manage them) to those situations

Except, however, the provisions for sludge dryers, carbon regeneration units, infrared incinerators, and plasma arc incinerators are not promulgated under HSWA authority.

where the unit becomes newly regulated in absence of a new waste identification. (See 53 FR 37922, September 28, 1988.) EPA believes that the same rationale applies to newly regulated types of units, and is therefore clarifying this provision in today's rule.

Without the procedure in §270.42(g), the facility would need to obtain an approved permit modification if the facility were to continue managing hazardous wastes past the effective date of today's rule, which establishes management standards for boilers and industrial furnaces. If the modifications were not approved within six months, these facilities would be barred from handling hazardous wastes, disrupting the ongoing operations of many of these facilities as well as other RCRA facilities that would then need to manage the wastes. As discussed below, EPA believes that the addition of a boiler or industrial furnace to a facility's permit is a Class 3 modification. Because of the time allowed for preparation of the modification request by the facility and public participation in the permit modification procedures, the Agency would be unable to review and make a final determination on the modification request in the six month period.

Today's technical correction rectifies a potential inequity between permitted facilities and newly regulated facilities. Newly regulated facilities are required only to submit Part A of the permit application, and submit the RCRA section 3010 Notification form, if necessary, to obtain interim status. Both activities can be easily completed by the effective date of today's rule, allowing them to continue operations, while permitted facilities, who have undergone the scrutiny of the permitting process, would likely be barred from doing so.

2. Procedures to Modify Permits. Under today's new procedures in §270.42(g), a unit that is "in existence" as a unit by managing hazardous waste on or before the effective date of today's rule must submit a Class 1 modification by that date. Essentially, this modification is a notification to the Agency that the facility is managing hazardous wastes in these newly regulated units. It could consist of a revised Part A application form clearly indicating all activities that are newly regulated as a result of today's rule. As part of the Class 1 procedure, the permittee must also notify the public regarding the modification within 90 days of submittal to the Agency.

Next, within 180 days of the effective date, the permittee must submit a Class 2 or 3 modification request to the Agency. It is at this time that the detailed Part B information must be submitted. The Agency believes that the Class 3 permit modification procedures are most likely applicable to the addition of boilers or industrial furnace units. The Class 3

modification requires an initial public notice by the facility owner of the modification request, a 60 day public comment period, and an informal meeting between the owner and the public within the 60 day period. After the end of the 60 day public comment period, the Agency will develop a draft permit modification, open a second public comment period of 45 days and hold a public hearing. After the public comment period, the Agency will make a final decision on the modification request.

Today's rule also amends Appendix I to §270.42 to classify the permit modifications for boilers and industrial furnaces. Section L is revised to include boilers and industrial furnaces with incinerators, and to specify additional permit conditions to conform with today's rule (and the conditions added to incinerator permits under the omnibus authority of §270.32(b)(2). For more information on these permit modification procedures, see 53 FR 37912, September 28, 1988.

# D. Addition of Storage Units at Direct Transfer Facilities That Obtain Interim Status

As discussed in section XII.C of Part Three of this preamble, the requirements for boilers and industrial furnaces are being promulgated under section 3004(q) of RCRA, which is a HSWA provision. As a result, under section 3006(g), EPA will implement these requirements in both authorized and unauthorized States until the State is authorized to implement these requirements in lieu of EPA. Based on comments received during the rulemaking, EPA is aware that many interim status facilities newly-regulated under this rule may wish to add storage units to their facilities in the future rather than continue direct transfer operations (direct firing of the burner from the transport vehicle). Furthermore, EPA recommends that facilities install tanks and reduce or eliminate direct transfer practices because of the additional hazards associated with the practice. As discussed in more detail below, EPA believes that such units can be added to the facility without awaiting complete permitting.

1. Unauthorized States. Facilities that wish to shift to storage from direct transfer operations and that are located in unauthorized states, will generally be able to add such units to the facility as a change in interim status under 40 CFR 270.72(a)(3). In order to qualify for addition of units under this provision, the facility must: (1) obtain interim status for the boiler or industrial furnace; and (2) submit a revised Part A application to the EPA Regional Office prior to adding the storage units with a justification for the change. Because EPA strongly encourages the discontinuation of direct transfer operations at boilers and industrial furnaces, EPA believes that the addition of storage units at such

facilities constitutes a change necessary to meet federal requirements under 40 CFR 270.72(a)(3)(ii). The Regional Office must approve the interim status change, unless it is covered by amended \$270.72(a)(6) just discussed. Although 40 CFR 270.72(b) limits the extent of an addition that can be made during interim status, the addition of associated storage units under today's rule would be exempt from this limitation pursuant to \$270.72(b)(2).

2. Authorized States. Interim status facilities located in authorized states that wish to discontinue direct transfer operations will also generally be able to add such units to the facility pursuant to 40 CFR 270.72(a)(3). In states which are not authorized to implement the HSWA storage requirements for boilers and industrial furnaces, the procedure for adding storage units at new interim status boilers or industrial furnaces is the same as described above for facilities located in unauthorized states. Because EPA is implementing both the rule promulgated today and the associated storage requirements in such states, the federal rules governing changes in interim status apply to both the boilers and industrial furnaces and the addition of associated storage facilities.

In states which have been authorized to implement the HSWA storage requirements for boilers and industrial furnaces, facilities newly regulated under today's rule must comply with the authorized state requirements concerning the addition of associated storage units. In some cases, the authorized state may require the facility to obtain a permit prior to constructing or operating such storage units.

#### E. Compliance with BIF Versus Incinerator Rules.

Existing rules (see §266.31(c)) require that cement kilns burning hazardous waste that are located in urban areas must comply with the hazardous waste incinerator standards. In addition, existing rules allow owners/operators of any boiler or industrial furnace to obtain an incinerator permit. These provisions exist because the Agency had not yet established regulatory controls for BIFs. In fact, the statutory provision (Section 3004(q)(2)(c)) requiring that cement kilns in urban areas be regulated as incinerators states that the "...regulations remain in effect until the Agency develops substantive standards for cement kilns burning hazardous waste." Therefore, on the effective date of the BIF rule, both of these regulatory provisions will be rescinded except as discussed below.

Commenters questioned what regulations should more appropriately apply under three scenarios: (1) if a BIF is operating in interim status under the Subpart O, Part 265,

incinerator standards; (2) if a BIF has already been issued an incinerator operating permit under Subpart O. Part 264; and (3) if a BIF has previously submitted a Part B application for an incinerator permit and the permit review process has progressed substantially by the effective date of the BIF rule. A BIF currently operating under the interim status incinerator regulations must comply with the BIF regulations on their effective date in lieu of the incinerator regulations so that it is subject to the more stringent BIF rule. A BIF currently operating under an incinerator permit will continue under that permit until it is reviewed or the permit term otherwise expires. At that time, the BIF rule will apply. Although the Agency's general policy is that BIFs are to be regulated only under the BIF rules, we believe permit officials should use their discretion to determine whether to grant exceptions for the third situation given the protectiveness of the standards, and the desirability of avoiding further delay and expense by having to duplicate the permit process under these BIF rules. For example, if a BIF is operating under the incinerator interim status standards but has submitted Part B of the incinerator permit and the permit proceedings have progressed substantially, the Director may continue processing the permit (and issue it) under the incinerator standards and use omnibus authority<sup>81</sup> to add conditions to the permit as necessary to conform with the BIF rule.

#### IX. Permit Procedures

#### A. Part B Information

As proposed on May 6, 1987 (52 FR 17015), § 270.22 provides specific information requirements for Part B of the permit application. Paragraph (a) requires a trial burn to demonstrate conformance with the performance standards of §§266.104 through 266.107, except where the trial burn is waived. Although the regulatory language is substantively the same as proposed, it has been restructured for clarity, by specifying the documentation required to support a waiver from each type of trial burn: DRE trial burn, particulate matter trial burn, metals trial burn, and HCl/Cl<sub>2</sub> trial burn.

In addition, the rule specifies under §270.22(a)(6) that owners and operators may submit data from previous compliance testing of the device, or from testing of similar

EPA notes that permit writers choosing to invoke the omnibus permit authority of §270.32(b)(2) to add conditions to a RCRA permit must show that such conditions are necessary to ensure protection of human health and the environment and must provide support for the conditions to interested parties and accept and respond to comment. In addition, permit writers must justify in the administrative record supporting the permit any decisions based on omnibus authority.

boilers or industrial furnaces burning similar wastes, in lieu of a trial burn provided that the data is determined adequate and sufficient documentation of similarity is provided.

Paragraphs (b) through (d) were added to \$270.22 to provide information requirements related to other regulatory provisions being promulgated today for boilers and industrial furnaces. Paragraph (b) requires information describing the automatic waste feed cutoff system. Paragraph (c) requires owners and operators using direct transfer operations to feed hazardous waste from transport vehicles directly to the boiler or industrial furnace to submit information supporting conformance with the direct transfer standards at § 266.111. Under paragraph (d), owners and operators that claim their residues are excluded from regulation under § 266.112 must submit information adequate to demonstrate conformance with those provisions.

#### B. Special Forms of Permits

As proposed, the final rule adds § 270.66 to Subpart F of Part 270. This section establishes special forms of permits (see discussion below) for new boilers and new industrial furnaces, and sets forth requirements for the various periods of operation under which a boiler or industrial furnace operates, depending on applicable trial burn requirements. This section also establishes trial burn procedures. Finally, this section discusses special procedures for permitting existing facilities. Although these provisions were described in the preamble to the proposal, at 52 FR 17016, they are described briefly below, in order to highlight minor changes from the proposed requirements.

1. Permits for New Boilers and Industrial Furnaces. Paragraph (b) specifies four operating periods of a permit for a new facility. The provisions have been restructured from those proposed in recognition of the fact that all boilers and industrial furnaces subject to a permit must undergo some type of trial burn. Although a facility could conceivably meet the requirements for a waiver of the DRE trial burn, particulate matter trial burn, metals trial burn, and HCl/Cl<sub>2</sub> trial burn, all regulated facilities must demonstrate conformance with the carbon monoxide, and where applicable, hydrocarbon limits of §266.104.

In addition, minor revisions to this section have been made to make the permit process for new boilers and industrial furnaces consistent with the way the hazardous waste incinerator permitting process is implemented, i.e., one permit with four periods of operations rather than an individual permit for each period of operation.

Thus, the final rule provides for permits addressing four periods of operation for all boilers and furnaces: the pre-trial burn period, the trial burn period, the post-trial burn period, and the final permit period.

Conditions addressing compliance with each performance standard (or corresponding waiver requirement) will be set in the permit for each period of operation. Applicants must submit a statement with Part B of the permit application that suggests the conditions necessary to operate in conformance with the performance standards of §\$266.104 through 266.107. For those performance standards for which a trial burn is required, the Director will use his engineering judgment, and consideration of the applicant's proposal, in setting operating conditions in the permit sufficient to meet the performance standards. Once the trial burn data are available, they will be used to modify, if necessary, the final operating conditions in the permit. For those performance standards for which a trial burn demonstration is not required (for example, when the applicant has chosen to comply with Tier I of the metals limitations under § 266.106(b)), appropriate conditions (in the above example, metals feed rate limits specified under § 266.102(e)(4)) will be set for all periods of operation.

The pre-trial burn period begins with initial introduction of hazardous waste into the boiler or industrial furnace and extends for the minimum time required, not to exceed 720 hours of hazardous waste burning, to bring the device to a point of operational readiness to conduct a trial burn. This period may be extended once by the Director if good cause is shown. The trial burn period covers the period when the trial burn is conducted. This period is followed by the post-trial burn period, which extends for the minimum time necessary to allow analysis, data computation, and submission of the trial burn results and modification of the permit by the Director if necessary to reflect the trial burn results. Such modifications will proceed under the permit modification provisions at § 270.42.

Paragraph (c) specifies information that must be included in the trial burn plan. Paragraph (d) establishes trial burn procedures, including criteria for approval of trial burn plans and requirements for submission of trial burn data. Paragraph (e) establishes procedures for selection of POHCs when a DRE trial burn is required. Finally, paragraph (f) establishes the determinations that the applicant must make based on the trial burn results -- the data, analyses, and computations that must be submitted to support conformance with the applicable emissions standards.

2. Permit Procedures for Interim Status Facilities. Applicants owning or operating existing boilers or industrial furnaces will be permitted under § 270.66(g). This paragraph addresses submission of trial burn plans and trial burn data for existing boilers and furnaces. These provisions differ from the proposal in that they specifically require that the applicable trial burn data be submitted and considered prior to permit issuance. This language conforms with the January 30, 1989 change to the hazardous waste incinerator regulations, promulgated at 54 FR 4286 providing clarification of this point.

# X. Exemption of Small Quantity Burners

Section 3004(q)(2)(B) of RCRA provides EPA with explicit authority to exempt from regulation facilities that burn small quantities of hazardous wastes if the wastes are burned at the same facility at which they are generated. The Administrator is to ensure that such waste fuels are burned in devices designed and operated in a manner sufficient to ensure adequate destruction and removal to protect human health and the environment.

The Agency has carefully evaluated the risks posed by small quantity burning and concluded that a conditional exemption for small quantity burners should be allowed where hazardous waste combustion poses insignificant risk. A discussion of the original May 1987 proposal and the subsequent October 1989 proposed revisions is presented below.

On May 6, 1987 (52 FR 17034), the Agency proposed to exempt facilities that burn small quantities of hazardous waste that they generate on site because even in the absence of regulatory control, the health risk posed by such burning would not be significant. Eligibility for the exemption would have been based on the quantity of waste burned per month, established as a function of device type and thermal capacity. In order to be exempt, in addition to restricting the quantity of waste burned, a facility was required to notify the Regional Administrator that it is a small quantity burner, limit the maximum instantaneous waste firing rate to 1% of total fuel burned, and refrain from burning acutely toxic waste containing dioxin.

On October 26, 1989 (54 FR 43730), the Agency proposed several revisions to the exemption in the 1987 notice. Rather than establish hazardous waste quantity limits as a function of device type and capacity, EPA proposed quantity limits that vary as a function of effective stack height. The exempt quantities proposed in October 1989, and promulgated today, include several changes to the risk assessment methodology. In particular, the quantities are based on evaluation of risks from hydrocarbon (HC) emissions

instead of a PIC/POHC ratio as originally proposed. This change was made to better account for organic emissions from combustion. In addition, the procedures for evaluation of facilities with multiple stacks were revised to reduce over-regulation in these situations.

#### A. Response to Comments

Numerous commenters to the 1987 and 1989 proposals objected to the conservatism of the calculated quantity limits and/or the 1% limit on hazardous waste firing. The commenters stated that the assumptions used in calculating the exempt limits are overly conservative, and that the 1% limit on firing of hazardous waste is based on unrealistic and unjustifiable conclusions. The commenters, however, did not provide data or analysis to support their arguments that assumptions used in the small quantity burner exemption (SQBE) calculations and conditions (including limits on the waste to be burned) for exemption eligibility were too restrictive. Absent technical support for alternate approaches, the Agency continues to believe that the approach proposed in October 1989 is reasonable and appropriate. In addition, using less conservative assumptions to derive the exempt quantities could allow relatively large amounts of hazardous waste to be burned, a result somewhat at odds with the statutory language referring to small "quantities" of hazardous waste. See §266.108(a)(2) which limits the maximum hazardous waste firing rate at any time to 1% of the total fuel requirements of the device on a volume basis. See also §266.108(a)(3) which requires the hazardous waste to have a minimum heating value of 5,000 Btu/lb, as-generated, to ensure that the exemption is limited to fuels as intended by section 3004(q)(2)(B) and to ensure adequate destruction of toxic organic constituents.

One commenter requested credit for the presence of air pollution control devices (APCDs). The Agency believes that it is not appropriate to allow credit for APCDs because, without requirements for and oversight of the operation and maintenance of the devices, there is no assurance that collection efficiencies are being met.

Four commenters to the 1987 proposal urged EPA to delete the small quantity burner exemption. These commenters were concerned that the large number of boilers and industrial furnaces burning hazardous waste that do not have to meet any design requirements would have a detrimental effect on human health and the environment. The Agency continues to believe that the exemption is protective of human health and the environment because it is health-based, incorporating quantity limits and conservative assumptions designed to be protective regardless of size and location of the device, or conditions of operation.

Two commenters stated that the exemption should apply to facilities that generate hazardous waste at off-site facilities under the same ownership and operational control. The Agency is concerned, however, that contrary to Congress's intent, this approach could allow a large quantity generator to distribute their hazardous wastes in small quantities to TSDFs (including entities that are parent corporations, joint ventures, subsidiaries of the generator, etc.) that would then burn the wastes without regulation. Consequently, the final rule limits the exemption to facilities that burn only hazardous waste generated on-site.

One commenter to the 1987 proposal urged the Agency to clarify that the 1% limit on the hazardous waste firing is to be applied only to unmixed hazardous waste fuel, not to a mixture of hazardous and non-hazardous fuel. The Agency acknowledges the ambiguity in the proposed rule language and intended the proposal to require that the quantity determination take into account only the hazardous waste fuel prior to mixing with a nonhazardous waste fuel. Today's final rule contains language to that effect and requires the exempt facility to keep records to document that the quantity of hazardous waste prior to mixing with a nonhazardous fuel complies with the quantity limitations.

Six commenters to the 1989 proposal suggested that quantity limits be based on 1% of the total fuel burned and not the stack height, which relies upon dispersion only. The Agency, however, continues to believe that terrain-adjusted stack height is the important criterion, because it is possible that even a 1% limit, with large dispersion and low stack height, could pose a threat to human health and the environment.

# B. Basis for Today's Final Rule

In order to calculate allowable exempt quantities under today's rule, worst-case dispersion coefficients (based on incinerator modeling), and an HC unit risk factor of 2 x  $10^{-5}$  m<sup>3</sup>/ug (based on a  $10^{-5}$  risk limit) were assumed, as proposed in the October 1989 supplemental notice. Allowable emission rates of hydrocarbons (HCs) were then back-calculated as a function of effective stack height, terrain type, and land use. The assumption used in this back-calculation was an HC concentration in the stack gas of 150 ppmv at 99.99% DRE. Finally, the exempt quantities were calculated using the HC emission rates and an empirically-derived ratio of combustion gas volume to mass of waste. The most conservative allowable emission rates calculated for each stack height were then used as the established quantity limits.

A detailed description of the methodology used to derive quantity limits for the exemption is available in the docket for the supplemental notice.

As mentioned above, the use of effective stack height to determine eligible quantity limits reflects one of the revisions proposed in the October 26, 1989 supplemental notice. The Agency notes that we have not established separate exempt quantity limits for the different terrain types and land use classifications. Rather, the revised quantities are based on assumptions of terrain and land use that result in the lowest (i.e., most conservative) exempt quantities. We believe that this conservative approach is appropriate given that there would be no EPA or State agency oversight of an operator's determination of a facility's terrain and land use classification. Some key assumptions used to arrive at the quantity limits are described below.

EPA evaluated the risks posed by emissions of organic compounds, metals, and hydrogen chloride, the parameters controlled in the substantive regulations promulgated in today's rule.<sup>82</sup> The analysis demonstrates that the risks posed by organic emissions from waste-as-fuel activities are overwhelmingly dominated by the risks posed by carcinogenic (as opposed to noncarcinogenic) waste constituents. Accordingly, the initial evaluation performed in support of the small quantity burner exemption focused exclusively on carcinogenic risks, on the assumption that controls ensuring insignificant risks from organic carcinogenic emissions will ensure protection against non-carcinogenic releases. This assumption was confirmed by evaluating the potential risks from metals and hydrogen chloride that would result when those quantities of waste indicated by the risk analysis for organic carcinogens were burned.

The risks from burning small quantities of hazardous waste are determined primarily by the following factors:

- Composition of the waste stream being burned;
- Toxicities and concentrations of hazardous constituents in the waste stream;
- Destruction and removal efficiency achieved by the device;
- Local meteorology, which influences the amount of dispersion of stack emissions;
- Clustering and size of sources; and
- The effective stack height of the device.

U.S. EPA, "Analysis for Calculating a de Minimis Exemption for Burning Small Quantities of Waste in Combustion Devices", August 1989.

The values of these parameters can and do vary widely. Reasonable, worst-case assumptions were made for these parameters in the Agency's calculations of exempt quantities and evaluation of risks. In the risk analysis, EPA assumed an acceptable cancer risk level of 1.0 x 10<sup>-5</sup> to an individual residing for 70 years at the ground level point of maximum exposure to reasonable, worst-case stack emissions. Reasonable, worst-case dispersion coefficients based on effective stack heights were used. The dispersion coefficients were those developed in the risk analysis for the proposed amendments to the hazardous waste incinerator regulations (See 54 FR 43752 and 55 FR 17871). The dispersion coefficients differ by terrain type, land use, and effective stack height. Separate calculations were made for noncomplex and complex terrain and urban and rural land use, resulting in three different sets of quantity eligibility limits for each effective stack height. The rationale for the assumptions used in the risk analysis is discussed below.

1. Composition of Hazardous Waste Stream. Composition data on hazardous waste-derived fuels is scarce. Information gathered by the mail questionnaire survey and other industry contacts indicate that most of the materials burned are organic solvents that are usually classified as hazardous based on ignitability and/or toxicity. The actual concentrations of carcinogens in wastes burned by 21 facilities during EPA's field testing program for boilers and industrial furnaces ranged from 0 to 17% with an average of approximately 4%.

The quantity of PICs measured in EPA test burns was found to be independent of specific POHC species and was a function of hydrocarbon (HC) content of the fuel only. This is supported by comparisons made by MRI of PICs from hazardous waste and fossil fuel combustion. Since it is impossible to differentiate between the PICs from fuel and those from hazardous waste during most tests, it was assumed that the boilers in the EPA test burns were using fuels of 100% HC and all PICs are the result of hazardous waste burning. Additionally, HC emissions are presumed to be an acceptable measurement of PICs; historic data indicate that HC measures from 75 to 95% of all PICs emitted.

The hazardous waste was assumed to contain concentrations of cadmium, chromium, nickel, and lead that were obtained from the state sampling reports of the Keystone Cement Company. Arsenic, barium, and mercury concentrations were based on 90th percentile levels from the Engineering Science Background Document.

- 2. Toxicity of Hazardous Constituents. The average unit risk of those PICs that were identified during EPA trial burns was  $1.0 \times 10^{-5}$  m<sup>3</sup>/ug. However, it is likely that the PICs resulting from incineration under the 99% DRE assumption for the small quantity burner analysis would have a higher toxicity than those measured under the 99.99% DRE in the EPA boiler tests. EPA therefore estimates the unit risk for total HCs to be  $2.0 \times 10^{-5}$  m<sup>3</sup>/ug. This corresponds to a carcinogenic potency of  $Q_1^* = 0.07$  for hydrocarbons (HC). As explained in the October 1989 notice, this potency factor was used rather than a  $Q_1^*$  value of 1.0 for products of incomplete combustion as originally proposed in the May 6, 1987 proposed rule because the Agency was concerned about possible nonconservative features of PIC estimation. (See 54 FR 43730).
- 3. Destruction Efficiency. The burner destruction efficiency determines the quantity of unburned hazardous wastes that will be emitted from the stack. Assumed values for boiler and furnace performance were selected based upon a review of test data generated in support of this rule and based on the professional judgment of Agency staff members familiar with the destruction and removal efficiencies (DRE) typically achieved by boilers. It was assumed that, in the worst case, boilers and furnaces would only achieve 99% DRE<sup>83</sup> of organic constituents. This represents a very poorly performing combustion device. In fact, as explained previously, most boilers and furnaces can be expected to achieve 99.99% DRE of organic waste constituents even when operated under less than optimal conditions.
- 4. Assumptions Regarding Metals and Chlorine in Waste Fuels. A similar reasonable, worst-case analysis was performed to evaluate the potential risks posed by emissions of toxic metals (including carcinogens) and hydrogen chloride from small quantity burners. As a result, it was determined that, at the volume cut-offs specified by the exemption and the assumed waste concentrations as discussed above, metals emissions caused by cofiring of hazardous wastes would not pose a significant risk. The analysis also considered hydrogen chloride emissions assuming a chlorine content of 50% in the hazardous waste fuel. The chlorine content in actual hazardous wastes seldom exceeds 3%; however, the highest chlorine content measured in a hazardous waste fuel fired in a boiler

We note that we assumed 99% DRE to derive the small quantity burner exempt quantities rather than the 99.9% that the owner/operator must assume under the low risk waste exemption of §266.109 because monitoring of CO is not required for the small quantity burner exemption to ensure that good combustion conditions are maintained. CO monitoring is required under the low risk waiver of the DRE trial burn.

of which EPA is aware was 43%. Predicted ground level concentrations of HCl also did not exceed the reference air concentrations.

The assumptions used to determine the effect of local meteorology/dispersion and the clustering of sources (stacks at the facility) are discussed in the following section.

#### C. How the Exemption is Implemented

- 1. Use of Terrain-Adjusted Effective Stack Height. In the 1987 proposal, the Agency used a set of assumptions about local meteorology, dispersion modeling, terrain conditions, etc., to determine eligible quantity limitations. As mentioned above, today's rule uses terrain-adjusted effective stack height along with the most conservative assumptions of terrain and land use to determine quantity limits for exemption eligibility. See §266.108.
- 2. Multiple Stacks. As explained in the October 1989 notice, in today's final rule the exempt quantities for a facility with multiple stacks from boilers or industrial furnaces burning hazardous waste are limited according to the following equation:

$$\sum_{i=1}^{n} \underbrace{Actual Ouantity Burned_{(i)}}_{1.0} \leq 1.0$$
i = 1 Allowable Quantity Burned\_{(i)}

#### Where:

- N means the number of stacks
- Actual Quantity Burned, means the waste quantity per month burned in stack "i"
- Allowable Quantity Burned, means the maximum allowable exempt quantity for stack "i"

For example, if a site had two stacks with effective stack heights (ESH) of 30 and 10 meters, the following equation would hold:

$$\frac{X}{140} + \frac{Y}{40} \leq 1.0$$

Where:

- 140 and 40 are the exempt quantities from §266.108 for stack heights of 30 and 10 meters, respectively
- X is the waste quantity burned in the device with the 30 meter stack
- Y is the waste quantity burned in the device with the 10 meter stack

In this example, if Y is burning 15 gallons/month, then X could burn no more than 87.5 gallons/month.

# D. Wastes Ineligible for Exemption

Boilers and furnaces burning hazardous waste fuels containing or derived from any of the following dioxin-containing hazardous wastes are not eligible for the exemption: EPA Hazardous Waste Nos. F020, F021, F022, F023, F026, and F027. See §266.108(a)(4). Given the toxicity of these wastes, EPA does not believe it is appropriate to exempt facilities burning them from regulation. Hazardous waste fuels containing or derived from these dioxin-containing wastes must be burned at a 99.9999% destruction and removal efficiency (DRE). We cannot expect boilers and furnaces to achieve that level of DRE when operating outside of the Agency's regulatory system.

### E. Exemption of Associated Storage

Hazardous fuel storage practices prior to burning vary from site to site. Many facilities burning relatively large quantities of hazardous waste fuels hold the fuels in a storage system and then pump the waste fuels through a dedicated line into the combustion zone of the boiler. Other facilities mix hazardous waste fuels with other fuels (typically virgin fuel oil) in a storage/mixing tank prior to burning the blended material. These tanks are not feasibly emptied of hazardous waste every 90 days and so are in most cases ineligible for the generator accumulation provisions in §262.34.

Under today's rule, facilities storing unmixed hazardous waste fuels are responsible for complying with all applicable standards for the storage of the hazardous waste fuel. Owners and operators that are eligible for the small quantity burner exemption and who mix toxic hazardous waste fuels with other fuels would, however, be exempt from the storage

standards after such mixing, as proposed. See \$266.101(c)(2). The basis for this exemption is discussed below.

The Agency is promulgating an exemption for storage of such storage/mixing tanks (for small quantity burners) in order for the small quantity burner exemption in Section 3004(q)(2)(B) to have practical application. Congress evidently envisioned a class of facilities capable of burning small amounts of hazardous wastes safely absent regulation and viewed such burning as a superior means of managing these small amounts of waste. Furthermore, assuming that small quantity waste storage is conducted safely, the Agency assumes that Congress also envisioned exemption of the storage since permitting storage would discourage safe on-site burning just as much as regulating the burning itself.

We believe that storage of small amounts of hazardous wastes mixed with virgin fuels would pose no significant incremental risks over storage of the virgin fuels. The monthly volumes of hazardous waste fuel covered by the small quantity burner exemption, for example, represent less than 1% of the fuel flow rate through these tanks. Under these circumstances, we think the statutory exemption can reasonably be read to encompass this limited class of storage practices as well.

We note further that the Agency is studying other situations where hazardous waste-containing mixtures may not be appropriately subject to regulation and will consider whether to issue rules addressing the issue generically. It appears to us justifiable to address the question for the limited class of burning facilities in advance of other types of situations because Congress has singled out small quantity burning facilities for exemption where appropriate. We note further that to the extent these small quantity waste-virgin fuel tanks are underground storage tanks (as defined in section 9001(1)), they would be subject to regulation under Subtitle I if they contain petroleum.

#### F. Notification and Recordkeeping Requirements

As proposed in the October 26, 1989 supplemental notice, the final rule requires (conditionally) exempt small quantity burners to provide a one-time written notification to EPA (see §266.108(c)) of their status as a small quantity burner and a certification that they are in compliance with the requirements of §266.108. To assist enforcement efforts, the owner or operator must also indicate in the notification the maximum allowable quantity that may be burned per month as provided by §266.108(a)(1). In addition, the final rule requires small quantity burners to keep records to document that they comply with the

conditions of the exemption including: quantities of hazardous waste burned per month; quantities of hazardous waste and other fuels burned at any time to demonstrate conformance with the 1% hazardous waste firing rate limit; and heating value of the hazardous waste.

# XI. Exemption of Low-Risk Waste from DRE Standard and Particulate Matter Emission Standard

The final rule defines two types of "low-risk" wastes: (1) waste that is low risk with respect to feed rate of hazardous (i.e., Appendix VIII, Part 261) nonmetal constituents and, thus, is exempt from the requirement to demonstrate 99.99% DRE; and (2) waste that is low risk with respect to both nonmetal constituents and metals (i.e., the waste meets the Tier I feed rate limits for metals provided by \$266.106(b)) and, thus, is exempt from both the DRE standard and the 0.08 gr/dscf particulate standard. See §266.109.

The following sections explain these exemptions and how they operate.

# A. Exemption from Compliance with the DRE Standard

In the May 6, 1987 proposed rule, the Agency proposed a risk-based, site-specific waiver of the DRE trial burn and the flue gas CO limits for facilities burning waste that poses insignificant health risks absent those controls (52 FR 17002). Today's final rule retains the exemption from the DRE standard, but requires the facility to monitor CO continuously and to comply with the Tier I PIC controls of §266.104(b) (i.e., CO cannot exceed the 100 ppmv limit on an hourly rolling average basis).

In the 1987 proposal, EPA explained the basis for the DRE exemption for boilers or industrial furnaces that burn low-risk waste (52 FR 17002). After further consideration, however, the Agency believes that controls on emissions of PICs are needed. This is because a waste with low levels of toxic organic constituents can nonetheless pose significant health risk if it is burned under poor combustion conditions conducive to formation of PICs. Toxic PICs can form from poor combustion of nontoxic organic compounds.

The final rule does not allow a burner to operate under the alternative CO limit provided by \$266.104(c), which allows higher CO levels provided that HC levels do not exceed 20 ppmv, because the Agency believes that only those devices operating under best demonstrated technology combustion conditions should be granted an exemption from the

DRE requirement. (We note that this is consistent with the CO restriction for the automatic waiver of the DRE trial burn for boilers operating under the special operating conditions provided by §266.110.) Devices operating at CO levels above 100 ppmv on an hourly rolling average are not operating under best demonstrated technology combustion conditions even if they can show that hydrocarbon levels do not exceed 20 ppmv (or the HC limit established under §2666.104(f)). As discussed at proposal (see 54 FR 43723 c.3), the 20 ppmv HC level represents a demarcation between good and poor combustion conditions. HC levels under best demonstrated technology combustion conditions would generally be less than 5 ppmv on an hourly rolling average basis.

#### B. Exemption from Compliance with the Particulate Standard

Today's final rule also provides a waiver of the particulate standard for facilities that both obtain the DRE standard waiver and meet the Tier I requirements for all metals. (Because the PM standard guards against risks from both adsorbed organic compounds and metals, only facilities with waste that is low risk for both organic constituents and metals are eligible for the PM waiver.)

The basis for imposing a particulate standard on boilers and industrial furnaces firing hazardous waste, as explained in the October 26, 1989 supplemental notice (54 FR 43719), is primarily the concern over adsorption of toxic organics and metals onto the emitted particulates. Consequently, the Agency believes that an exemption from the particulate standard for boilers and industrial furnaces is appropriate provided that the facility can demonstrate that emissions of toxic organics and metals do not pose unacceptable human health risks.

#### C. Eligibility Requirements

Three eligibility requirements for the low-risk waste exemption were detailed in the 1987 proposed rule. Many commenters objected to the first of these requirements, that 50 percent of the fuel fired in the boiler or industrial furnace must consist of oil, natural gas, coal, or other fossil fuels derived from these fuels. These commenters requested that EPA allow the cofiring of various other fuels, including tall oil, off-specification fuel oils, and wood chips.

Although some of these fuels may provide a hot, stable flame that will support good combustion, the Agency is concerned that others may not. In today's rule, the Agency is requiring for this exemption the same conditions on the primary fuel as required for the

special operating requirements for boilers seeking the automatic waiver from a DRE trial burn (see section II.A.3 of Part Three of this preamble): a minimum of 50% of the fuel fired to the boiler must be high quality "primary" fuel consisting of fossil fuels or fuels derived from fossil fuels, tall oil, or, if approved by the Director on a case-by-case basis, other nonhazardous fuel comparable to fossil fuel, and all such primary fuels must have a minimum as-fired heating value of 8,000 Btu/lb.

The two remaining eligibility requirements, that the hazardous waste must have an as-fired heating value of at least 8,000 Btu/lb, and that the waste must be fired into the flame zone of the combustion chamber, are being promulgated as proposed in 1987. The reasons for these requirements are the same as discussed in section II.A.3 of Part Three of this preamble in the context of the automatic waiver of the DRE trial burn for boilers.

# D. How the Low-Risk Waste Exemption Works

- 1. Constituents of Concern. The low-risk waste exemption is intended to exempt a waste from either or both the DRE standard and the particulate standard if the owner/operator demonstrates that, absent regulatory controls (i.e., under a reasonable, worst-case emissions scenario), emissions from the facility will not result in ambient levels of toxic organic compounds and/or metals that exceed acceptable levels. The organic constituents of concern are the hazardous organic compounds listed in Appendix VIII of 40 CFR Part 261 and the metals of concern are the 10 regulated metals. See section E of this preamble.
- 2. Estimation of Worst-Case Emissions. The requirements for estimating worst-case emissions were discussed in the May 1987 proposed rule and are being promulgated in today's rule with slight modifications.

To estimate reasonable, worst-case emissions of toxic organic constituents in hazardous waste fuel, an owner or operator must: (1) identify every nonmetal Appendix VIII constituent that could reasonably be expected to be found in the waste; and (2) assume a reasonable, worst-case destruction and removal efficiency (DRE) for each constituent of 99.9 percent in calculating the worst-case emissions (by considering waste concentration and feed rate) from the stack for each constituent. This assumed DRE of 99.9 percent is less conservative than the proposed 99 percent assumption in the 1987 notice. The Agency is making this change in response to the many commenters who objected to the 99 percent DRE assumption. Specifically, the commenters' objection was that 99.9 percent was the

worst DRE measured by the Agency in its nonsteady-state testing of boilers operated under intentionally upset (i.e., high CO and smoke) conditions. The Agency believes that changing the assumed DRE from 99 percent to 99.9 percent is justified because today's rule, unlike the 1987 proposal, does not provide a waiver of the continuous CO emission monitoring (CEM) requirements. Compliance with continuous CO monitoring requirements will ensure that these devices do not operate under upset conditions and will achieve a DRE of at least 99.9 percent.

The Agency has eliminated the proposed requirement that emissions of products of incomplete combustion (PICs) be estimated using a ratio of PICs to principal organic hazardous constituents (POHCs). As explained in the April 1989 notice (54 FR 43730), use of the PIC:POHC ratio may not be a conservative method for estimating PIC emissions.

An estimate of worst-case emissions is not necessary for metals. To be eligible for the exemption from the particulate standard, the waste must be low-risk with respect to organic compounds and must meet the Tier I metals feed rate limits. See §266.106(b). Those metals feed rate limits assume that all metals feed into the device are emitted.

- 3. Dispersion Modeling. Dispersion modeling must be used to predict the maximum annual average ground level concentration of each toxic nonmetal compound in the waste using procedures identical to those required to implement the Tier III metals controls. See 266.109(a)(2)(iii)(A).
- 4. Acceptable Ambient Levels. Predicted maximum annual average ground level concentrations of each toxic nonmetal compound may not exceed levels the Agency proposed as acceptable for purposes of this rule. The acceptable ambient concentrations were developed for carcinogenic and noncarcinogenic compounds using the same procedures used to develop the RACs and 10<sup>-5</sup> RSDs for the 10 toxic metals.

To demonstrate that the noncarcinogenic nonmetal compounds listed in Appendix IV of the rule do not pose an unacceptable health risk, the predicted ground level concentrations cannot exceed the levels established in that Appendix.

To demonstrate that the carcinogenic nonmetal compounds listed in Appendix V of the rule do not pose an unacceptable health risk, the sum of the ratios of the predicted ground level concentrations to the levels established in the Appendix cannot exceed 1.0. This is because the acceptable ambient levels established in Appendix V are based on a 10-5

risk level. To ensure that the summed risk from all carcinogenic compounds does not exceed 10<sup>-5</sup> (i.e., 1 in 100,000), the sum of the ratios described above must be used.

To demonstrate that other compounds for which the Agency does not have adequate health effects data to establish an acceptable ambient level are not likely to pose a health risk, the predicted ambient level cannot exceed 0.09 ug/m<sup>3</sup>. This is the 5th percentile lowest reference air concentration for the compounds listed in Appendix IV of the rule.

5. Constituents with Inadequate Health Effects Data. At the time of the 1987 proposal, the Agency had data adequate for establishing RACs and RSDs for only about 150 of the over 400 compounds listed in Appendix VIII, Part 261. In the preamble to the May 1987 proposal, EPA stated that, to be eligible for the exemption, health effects data (i.e., RACs and RSDs) must be available for each constituent in the waste. In response to comments concerning the inadequacy of current health effects data to establish a RAC or RsD for a large number of compounds, we have established in today's rule a conservative RAC value for such constituents determined as the 5th percentile lowest RAC for all of the nonmetal Appendix VIII, Part 261, constituents -- 0.09 ug/m<sup>3</sup> (see note to Appendix V of the final rule). EPA believes that this approach will be protective of human health and the environment and will not unreasonably restrict owners/operators from eligibility for the exemption.

#### XII. Storage Standards

#### A. Permit Standards for Storage

Under the administrative controls for hazardous waste marketers, burners, and blenders of hazardous waste burned in boilers and industrial furnaces promulgated on November 29, 1985, and codified in Subpart D of Part 266, EPA subjected existing burner storage facilities (effective May 29, 1986) to only the interim status standards of Part 265. The permit standards of Part 264 were not applied to existing storage facilities in order to avoid two-stage permitting, given that today's rule for permitting boiler and industrial furnace facilities was under development at that time. The Agency wanted to avoid requiring a boiler or industrial furnace owner or operator to obtain a permit for their hazardous waste fuel storage facility and to soon thereafter obtain another permit for operation of the boiler or industrial furnace under today's rule.

Today's rule does, therefore, subject such existing burner storage facilities to the permit standards of Part 264. See §266.101(c).

Numerous comments on the May 6, 1987 proposed rule to subject burner storage units to the permit standards of Part 264 agreed that the interim status standards currently in force are not adequate and permit standards are needed. Several commenters were concerned about the potential mishandling of waste fuels stored on-site in and around residential areas. One commenter requested that preburn transport and storage regulations for hazardous waste apply to all hazardous waste blends, mixtures, or diluted hazardous materials.

With the promulgation of today's rule, all hazardous waste storage units will be subject to applicable Part 264 and 265 standards. Since hazardous waste storage units standards are designed to be protective of human health and the environment regardless of the location of the facility, on-site storage associated with boilers and industrial furnaces burning hazardous waste is not restricted to areas in or around residential areas. These standards apply to the storage of any hazardous waste blends, mixtures, or dilutions that will be burned at these facilities, due to the "mixture rule" of 40 CFR 261.3. Whereas nonindustrial boilers were previously prohibited from burning hazardous wastes unless they were operated in conformance with the incinerator standards of Subpart O of Parts 264 or 265, today's rule eliminates the distinction between industrial and nonindustrial boilers. Consequently, today's rule establishes standards that are protective when hazardous waste is burned in any boiler.

One commenter recommended that the final rule allow the 90-day "on-site" accumulation provision to include wastes received at the BIF from off-site, company-owned locations. The 90-day accumulation provision referred to by the commenter is contained in 40 CFR 262.34(a) and only applies to generators of hazardous wastes. The Agency does not intend to apply this provision to hazardous waste treatment, storage, or disposal facilities.

#### B. Consideration of Requirement for Liquid Waste Fuel Blending Tanks

In the October 26, 1989 supplemental notice, the Agency requested comment on a requirement that all boiler and industrial furnaces use blending and surge storage tanks (i.e., other than other modes of waste fuel transfer) to avoid flow interruptions and waste stratification which could affect the ability of a combustion device to meet performance standards. The majority of commenters opposed requiring blending and surge storage tanks for BIFs and suggested that such a requirement would not be necessary to ensure

compliance with performance standards. Several commenters believed that a uniform requirement for tanks, containers, and/or surge tanks may not be universally appropriate. These commenters noted that some secondary materials such as lead acid batteries, flue dust, and various scraps and slags cannot be transferred to furnaces from a tank or container system. Another commenter suggested that in some instances, such as feeding incompatible wastes, direct transfer may be preferable due to health and safety concerns. A few commenters concurred with this view, but felt that storage and blending tanks should be required in all other instances. One commenter suggested that storage tanks should be required only if transport vehicles do not meet Department of Transportation requirements, secondary containment is not used in transfer operations, and if operations are not covered by site-specific contingency or SPCC plans. One commenter agreed that hazardous wastes should generally be fed from storage tanks and supported a final rule that would allow a "window of opportunity" to install storage tanks, thus providing an incentive for a company to reduce their reliance on direct burning from transport vehicles.

In today's rule, the Agency is not requiring storage and blending tanks for boilers and industrial furnaces burning hazardous waste because we continue to believe that such tanks are not requisite to demonstrating conformance with the emission standards of §§266.104 through 266.107. However, as indicated in the supplement to the proposed rule, EPA believes that facilities that install blending and storage tanks may be better able to control flow interruptions and waste stratification. Consequently, boilers and industrial furnaces with blending and/or storage tanks may operate with greater efficiency and thereby may more readily meet performance standards for emissions.

We also note that, once an owner/operator is in interim status, the Part A application may be revised to convert from direct transfer operations to the use of storage units. See discussion in section VIII of Part Three of the preamble.

#### C. Standards for Direct Transfer Operations

In the October 26, 1989, supplement to the proposed rule, EPA identified permitting authorities' concerns about the practice of feeding hazardous waste fuels directly from transport vehicles to boilers and industrial furnaces. These concerns included: (1) the potential for fires, explosions, and spills during transfer operations; and (2) the stratification of waste in the transport container and the potential for waste fuel flow interruptions which, in turn, could affect the ability of the burner to consistently provide efficient combustion of the waste. EPA requested comment on two approaches to regulate

direct transfer operations. One approach was for permit writers to use the RCRA omnibus authority to establish additional permit conditions as necessary to ensure adequate protection of human health and the environment from such operations. The other approach was to require that facilities burning hazardous waste use blending and surge storage tanks to avoid the flow interruptions and waste stratification, which would address permit writers' concerns.

In the April 27, 1990 Federal Register notice, EPA noted that commenters on the October 1989 notice stated that controls on transfer operations were needed during interim status. As a result, the Agency requested comment on the need and appropriateness of regulating direct transfer operations under interim status standards for containers and tank systems of Subparts I and J of Part 265. EPA received numerous comments in response to these solicitations. The majority of commenters recommended that EPA allow direct transfer with proper controls and restrictions, such as: (1) allow direct transfer approval for facilities granted interim status or a RCRA operating permit; (2) establish direct transfer standards similar to Subparts I and J of 40 CFR Part 265 for facilities with a contingency or SPCC plan; and (3) allow direct transfer during test burns alone. Some respondents suggested that instead of allowing direct transfer, EPA should require storage and blending tanks for all facilities burning hazardous waste.

The Agency is today promulgating standards regulating direct transfer operations. See §266.111. The Agency believes that these standards will adequately address potential risks to human health and the environment.

EPA considers direct transfer operations to be a part of the hazardous waste firing system, not a storage activity. Hence, facilities that are not subject to the burner standards of §§266.102 (permit standards) or 266.103 (interim status standards) are not subject to the direct transfer standards. Examples of facilities not subject to the direct transfer standards are small quantity burners exempt from regulation under §266.108, metals reclamation furnaces deferred under §266.100(c), and coke ovens exempt under §266.101(b)(4).

These direct transfer standards reference extensively the Subpart I container standards and the Subpart J tank standards of Parts 264 and 265 and will apply equally to facilities operating under a permit as well as those operating under interim status. The regulations address the area in which transport vehicles are located and piping and other ancillary equipment (termed "direct transfer equipment in today's rule) used to transfer waste from the vehicle to the burner. The standards provide general operating requirements

and controls on equipment integrity, containment and detection of releases, response to leaks or spills, design and installation of new direct transfer equipment, and closure.

- 1. General Operating Requirements. Facilities that directly transfer hazardous waste to boilers and industrial furnaces from transport vehicles must comply with general operating requirements that specify safe management practices for handling incompatible wastes, spill prevention controls, and automatic waste feed cutoffs. These general operating requirements apply to both containerized and bulk hazardous waste. General performance standards for safe operation in today's rule include measures for conducting direct transfer operations such that fire, explosion, violent reactions, and other conditions that could threaten human health or the environment do not occur. Direct transfer from open-top containers is prohibited. Direct transfer equipment, which is any device that distributes, meters, or controls hazardous waste flow between a transport vehicle and a BIF, must also be closed except when necessary to add or remove the waste. Safe management practices for handling incompatible wastes are also required. Transport vehicles or direct transfer equipment holding ignitable or reactive hazardous waste must be located at least 50 feet from the receiving facility's property line.
- 2. Inspections and Recordkeeping. All equipment and areas where direct transfer occurs must be inspected hourly for leaks during direct transfer operations. Control equipment, direct transfer equipment monitoring data, and other equipment ensuring compliance with direct transfer standards must also be inspected hourly. Finally, the rule provides recordkeeping requirements to document results of inspections.

We note that only daily inspection is required under Subpart J of Parts 264 and 265 for tank systems (i.e., piping, valves and other direct transfer equipment). EPA is requiring hourly inspections of direct transfer operations because, unlike tank systems that use hard piping, direct transfer operations use flexible hoses and quick change coupling devices that have a greater potential for leaks or spills.

3. Equipment Integrity. Equipment integrity requirements address direct transfer equipment (e.g., piping or conveyors from the transport vehicle to the burner). The standards promulgated today require the transfer of waste to other equipment if equipment holding hazardous waste leaks or is in poor condition, and specify safe management practices for transferring wastes to other containers or transport vehicles. An assessment is required of existing direct transfer equipment that does not meet the secondary containment requirements discussed below to determine if the direct transfer equipment is leaking or

unfit for use and must be certified by a qualified, registered professional engineer. If equipment is found to be leaking or unfit for use, the owner/operator must comply with the requirements addressing responses to leaks or spills.

- 4. Containment and Detection of Releases. The rule requires secondary containment for underground direct transfer equipment.. See §266.111(e)(1). Inspections and leak tests of direct transfer equipment and recordkeeping requirements are also required. Existing direct transfer equipment subject to the secondary containment requirements of §265.193 (by reference in §266.111(e)(1) of today's rule) must comply with those secondary containment requirements within two years after the effective date of the rule. EPA believes that two years (30 months from promulgation) is a reasonable amount of time to enable owners and operators to retrofit existing equipment with secondary containment as necessary given that direct transfer operations generally do not involve the use of extensive equipment subject to secondary containment.
- 5. Response to Leaks or Spills. Action required to be followed in the event of a leak or spill are based on those required in Subpart J, Part 265. See §266.111(e)(5). Should a leak or spill occur, equipment use must cease (to prevent the flow or addition of wastes into the direct transfer equipment or secondary containment system) and the system must be inspected to determine the cause of the release. The waste must be removed from the direct transfer equipment or secondary containment system and visible releases to the environment must be contained. In the event of a leak or spill, the Director must be notified of the incident in writing. Secondary containment, repair, or closure of the leaking equipment, and certification of major repairs must be provided.
- 6. Design and Installation of New Equipment. New direct transfer equipment must meet the design and installation standards specified in today's rule as defined in §265.192 for tank systems. See §266.111(e)(4) in today's rule referencing that section. The standards include: specifications for assessing the design of new direct transfer equipment; backfill requirements for new underground direct transfer equipment; tightness tests; equipment support and protection requirements; corrosion protection; and written certification that these requirements have been met.
- 7. Closure. Today's rule applies by reference the closure requirements for direct transfer equipment provided by §265.197 (except paragraphs (c)(2) through (c)(4)). See §266.111(e)(6). That section requires the removal or decontamination of waste residues, system components, and contaminated soils, structures, and equipment.

# XIII. Applicability of the Bevill Exclusion to Combustion Residues When Burning Hazardous Waste

Under the Agency's existing regulations, wastes that are derived from the treatment of listed hazardous wastes are also considered to be hazardous unless and until they are delisted (see 40 CFR 261.3(c)(2) and (d)(2)). The combustion or processing of hazardous waste in a device that uses elevated temperatures as the primary means to change the chemical, physical, or biological character or composition of the hazardous waste, is a type of treatment no matter what type of device is used in the process, or for what purpose the waste is burned or processed. Accordingly, under the Agency's existing rules, residues from thermal combustion (or processing) of listed hazardous wastes remain the listed hazardous wastes until they are delisted.

When the device burning hazardous waste is (1) a boiler burning primarily coal or other fossil fuels, (2) an industrial furnace processing primarily ores or minerals, or (3) a cement kiln processing primarily raw materials, the applicability of the Bevill exclusion must be considered (see RCRA Section 3001(b)(3)(A)(i-iii)). The Bevill exclusion refers to residues resulting from burning or processing certain materials whereby the residues are not considered to be hazardous waste at this time because they require special study to determine whether they should be regulated under Subtitle C.

To determine whether the Bevill exclusion continues to apply when the devices described above burn or process hazardous waste, today's final rule promulgates the case-by-case determination involving a two-part test as discussed in the October 1989 supplement to the proposed rule. See §266.112. Under this test, owners and operators must determine on a site-specific basis whether the co-combustion of hazardous waste has significantly affected the character of the residue. The residue is considered to be significantly affected if both: (1) concentrations of toxic (Appendix VIII, Part 261) compounds in the waste-derived residue are significantly higher than in normal (i.e., without burning/processing hazardous waste) residue; and (2) toxic compounds are present in the waste-derived residue at levels that could pose significant risk to human health. If the case-by-case determination demonstrates that the residue has been significantly affected (or if the owner or operator does not obtain data and information adequate to support a demonstration that the residue has not been significantly affected), such derived-from residues are subject to regulation as hazardous waste because the residues are no longer the type of material Congress commanded the Agency to study before regulation. Such

residues are no longer deemed to be from processing ores or minerals, burning fossil fuels, or making cement. Rather, they are from treating hazardous waste.

The following sections discuss the basis for applying the Bevill exclusion to derived-from residues, the evolution of the Agency's interpretations on the applicability of the Bevill exclusion to waste-derived residues, and how today's case-by-case determination works.

#### A. Basis for Applying the Bevill Exclusion to Derived-From Residues

A number of commenters questioned whether the Agency has the legal authority to determine that some residues from coprocessing hazardous waste with Bevill raw materials could remain excluded under the Bevill amendment pending completion of the section 8002 studies. Because the Agency's previous determination of this question (50 FR 49190 (Nov. 29, 1985)) could have been more fully explained, the Agency has decided to reopen the question in this rule and to respond to the public comments.

The Agency's consistent position on this issue is that so long as the processing of hazardous waste does not significantly affect the character of the waste residues as high volume/low hazard, then those wastes can remain excluded under the Bevill amendment. Put another way, the wastes can potentially remain the type of material that Congress told the Agency to study before imposing subtitle C regulation.

Instead of focusing on the question of whether coprocessing hazardous waste affects the composition of the residues from a Bevill device, some commenters would have it that the mixture and derived-from rules apply to the residues, so that the residues are subject to subtitle C (assuming listed wastes are coprocessed) regardless of the actual effect of burning hazardous waste. At the least, the statute does not compel this result. In the case of utility boilers burning fossil fuels, the statute states explicitly that wastes "generated primarily from the combustion of coal or other fossil fuels" is to be excluded. See section 3001(b)(3)(A)(i). Thus, some type of co-combustion is expressly authorized. With respect to the two remaining categories of Bevill waste (wastes from processing ores and minerals and cement kiln dust), the Bevill amendment (section 3001(b)(3)(A)) does not use the term "primarily", but does not expressly address the question of whether the exemption applies when the residues are produced in part from burning hazardous waste. Thus, read

literally, dust from a cement kiln that burns hazardous waste along with normal raw materials could be termed "cement kiln dust".84

If there were doubt on this point, the Agency is convinced that it is dispelled by the 1984 amendments. Sections 3004(q)(1) and 3010(a) both state explicitly that "(n)othing in this subsection shall be construed to affect or impair the provisions of section 3001(b)(3)" (the Bevill amendment). This language would be meaningless unless it allowed some residues from Bevill devices burning hazardous wastes (specifically hazardous waste fuels) to remain within the scope of the Bevill amendment. Although commenters argued, based on passages from the legislative history, that the provision should not be given this natural meaning, the Agency does not find the argument persuasive. Rather, the legislative history appears to state that Bevill devices burning hazardous waste fuels will be subject to the emission standards developed pursuant to section 3004(q). See H. Rep. No. 198, 98th Cong. 1st Sess. 41; S. Rep. No. 284, 98th Cong. 1st Sess. 37. Today's rules accomplish that result.

At the same time, the Agency is concerned about reading the Bevill amendment in a manner that gives it undue scope, such as by allowing Bevill devices to serve as a dumping ground for other hazardous wastes. We do not view the interpretation adopted today as allowing the exemption to have undue scope. In the first place, emissions from the Bevill device itself are regulated. Second, the facility becomes subject to the facility-wide corrective action provisions of sections 3008(h) and 3004(u) by virtue of regulation of the combustion activity. Thus, potential problems relating to mismanagement of waste residues must be evaluated and addressed no later than during the permitting process.

Most importantly, the Agency believes that the reading adopted strikes a reasonable balance between the terms of the Bevill amendment and other provisions and regulations relating to hazardous waste management. A reading that would disqualify residues from the Bevill amendment if any hazardous waste is burned in the device would exalt form over substance by barring from Bevill eligibility a residue that was not discernably affected by

EPA does not accept the argument that the omission of the word "primarily" in regard to ore/mineral processing wastes and cement kiln dust means that the residues must come exclusively from processing raw materials exclusively. This type of negative inference is not a compelled reading of the statute, and the legislative history to the provision in fact indicates that Congress used the term "primarily" with respect to utility wastes to overrule a 1978 EPA proposed regulation on the scope of utility wastes, rather than to affect the scope of the remaining two Bevill categories. 126 Cong. Rec. 3363 (1980).

burning hazardous waste. Given that such material could be exactly the high volume/low hazard residue that Congress told the Agency to study before regulating, EPA does not agree with an interpretation that automatically forecloses it from Bevill status. <sup>85</sup> In addition, use of Bevill devices for combusting hazardous wastes provides needed treatment capacity for a number of hazardous wastes, and the Agency would be reluctant to adopt an interpretation that discouraged safe processing of hazardous waste by necessarily imposing hazardous waste disposal costs on residues that might not be affected by the hazardous waste combustion.

For all of these reasons, therefore, the Agency is reading the statute in a way that does not automatically disqualify residues from coprocessing hazardous wastes in Bevill devices from eligibility for Bevill exempt status.

#### B. Evolution of Interpretations

To determine whether the Bevill exclusion continues to apply when the devices described above<sup>86</sup> burn hazardous waste fuel, the Agency stated in 1985 (see 50 FR 49190 (Nov. 29, 1985)) that the exclusion continues to apply as long as the hazardous waste is burned for energy recovery (i.e., not for destruction). The underlying principle for this determination was that when hazardous waste is used as fuel, the character of the residue would continue to be determined by the Bevill material (e.g., coal, ores or minerals, or cement raw materials) being burned or processed. Thus, the residue should remain within the Bevill exclusion pending special study before it could be regulated under Subtitle C.

In the May 6, 1987 proposed rule (52 FR 17012-013), the Agency suggested refining these determinations to address residues from industrial furnaces processing ores or minerals and that also process hazardous waste for materials recovery, and residues from cement kilns that may process hazardous waste as an ingredient. Under that proposal, such residues would remain within the Bevill exclusion provided that at least 50 percent of the raw material fed to the device consisted of a virgin ore, mineral, or normal

EPA notes that in assessing whether residues have been affected by hazardous waste burning it is using a somewhat more rigorous test for assessing inorganic contamination — use of the TCLP rather than the synthetic acid rain leaching procedure—than it used in making the high volume/low hazard determination for mineral processing wastes. 54 FR at 36630 (Sept. 1, 1989). The Agency views this as an additional safeguard to assess the possible effect coprocessing of hazardous waste may have had on the residues.

That is, a boiler burning primarily coal, an industrial furnace processing primarily ores or minerals, or a cement kiln processing primarily raw materials.

raw material. However, residues from devices burning hazardous waste for the purpose of destruction (i.e., for neither energy nor materials recovery) would not qualify for the Bevill exclusion.

The Agency has evaluated these interpretations of the applicability of the Bevill exclusion to waste-derived residues in light of its stated principle that residue that results from coburning hazardous waste and Bevill raw materials should remain within the Bevill exclusion provided that the character of the residue is determined by the Bevill material (i.e., the residue is not significantly affected by the hazardous waste). As discussed in the October 1989 supplement to the proposed rule (54 FR 43733-36), the Agency does not believe that its data base for making these interpretations is sufficient to ensure that, in every case, the residue would not be significantly affected by the hazardous waste. Further, the Agency has reconsidered whether the interpretation that residues generated by the subject devices when burning waste for destruction are not within the Bevill amendment is consistent with the stated principle. Consequently, the Agency proposed in the supplemental notice to require case-by-case determinations of the effect of burning hazardous waste on residuals. That case-by-case approach is promulgated in today's rule.

#### C. Case-By-Case Determinations

We discuss below which devices are eligible for the Bevill exclusion of residues and how the two-part test works for determining whether combustion of the waste has significantly affected the residue.

1. Eligible Devices. Until further studies were completed, Congress intended to exclude from Subtitle C regulation residues from: (1) devices that burn primarily fossil fuel; (2) industrial furnaces that process ores or minerals; and (3) cement kilns. As the Agency reads these provisions, to be eligible for exclusion from Subtitle C regulation under the Bevill amendment, the waste-derived residue must be generated from: (1) a boiler burning primarily coal<sup>87</sup>; (2) an industrial furnace processing primarily ores or minerals (otherwise, residues could not be said to come from processing ores and minerals, but rather from processing other materials), or (3) a cement kiln processing primarily raw

The Agency has determined that residues from cofiring hazardous waste with oil or gas are not excluded under the Bevill amendment because the character of the residue would be determined by the hazardous waste. This is because oil and gas generally produce little residue when burned and, thus, toxic constituents from the hazardous waste can significantly affect any residue generated. See 50 FR 49190 (Nov. 29, 1985). The Agency is not reopening this determination in today's rule.

materials. To implement the provision that, to be eligible for the Bevill exclusion the device must burn primarily Bevill material, EPA is requiring that a boiler must burn at least 50 percent coal, an industrial furnace must process at least 50 percent ores or minerals, and at least 50 percent of the feed stock to a cement kiln must consist of normal raw materials. This requirement also confirms the Agency's long-standing interpretation that the Bevill exclusion applies only to primary facilities and not to secondary facilities such as secondary smelters. See §266.112(a).

- 2. Two-Part Test. Today's rule requires a case-by-case determination as to whether the hazardous waste being burned or processed significantly affects the character of the residue with respect to inorganic and organic toxic (i.e., Appendix VIII, Part 261) constituents. The residue is considered to be significantly affected if both: (1) concentrations of toxic (Appendix VIII) compounds in the waste-derived residue are significantly higher than in normal (i.e., without burning/processing hazardous waste) residue; and (2) toxic compounds are present in the waste-derived residue at levels that could pose significant risk to human health. Part One of the test need not be conducted if the waste-derived residue passes Part Two of the test (i.e., if the health-based concentration limits are not exceeded). Such a waste would still meet the high volume/low hazard Bevill threshold.
- a. Part One -- Comparison with Normal Residues. Part One of the test requires a comparison of hazardous waste-derived residues with normal residues to determine if toxic compounds are present at statistically significant higher levels. See §266.112((b)(1). The toxic compounds of concern are any compound listed on Appendix VIII, Part 261, that may reasonably be expected to be a constituent in the hazardous waste plus the list (see Appendix VIII to the rule) of 31 organic compounds that are common products of incomplete combustion (PICs) from burning hazardous waste. The total concentration of each compound of concern in the residues is to be determined. Analytical procedures are provided in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846) incorporated by reference in §260.11(a).

In support of this reading, one court has held that residues from a secondary lead smelter are not covered by the Bevill amendment. Ilco Co. v. EPA (W.D. Ala. 1986).

We note that Part One of the test considers the total concentration of each compound, while Part Two of the test considers, for metals, the concentration in an extract generated from the Toxicity Characteristic Leachate Procedure (TCLP).

The rule requires the use of a statistical test to compare the concentrations of toxic constituents in samples of normal (without burning/processing hazardous waste) residues with samples of waste-derived residues. In the statistical test, the 95th percent confidence interval about the mean of the normal residue concentrations (using a "t" distribution) is used to determine the upper 95th percent confidence interval about the mean. Procedures that must be used to determine the upper 95th percent confidence interval about the mean are prescribed in "Statistical Methodology for Bevill Residue Determinations" in Methods Manual for Compliance with the BIF Regulation, incorporated by reference in §260.11(a). A minimum of ten composite samples must be obtained and analyzed to represent the normal residue in order to effectively calculate the upper 95th percent confidence interval about the mean. This is the concentration that the waste-derived residue may not exceed to pass Part One of the test. The waste-derived residue must be characterized by composite samples with a composite period not to exceed 24 hours to ensure that residues are managed properly and promptly (i.e., as exempt residues or hazardous waste) and to provide for effective enforcement. The sampling approach must be based on (and be consistent with) representative sampling protocols described in SW-846 and must be documented by recordkeeping.

If operating conditions change so that concentrations of toxic compounds in normal residue may (would have) decrease(d), the owner and operator must re-establish the "baseline" concentrations in normal residue and use the lower baseline levels for the test. This is necessary to ensure that owners/operators do not use the most contaminated raw materials in order to burn more hazardous waste, and then switch back to their normal raw materials.

b. Part Two.-- Comparison with Health-Based Limits. Part Two of the test requires a comparison of the concentration of toxic constituents in the waste-derived residues with health-based limits the Agency has established in Appendix VIII to the rule. The comparison is made to determine if toxic compounds in the waste-derived residue are present at levels higher than the health-based limits. The toxic compounds of concern are the same as for Part One of the test -- any compound listed on Appendix VIII, Part 261, that may reasonably be expected to be a constituent in the hazardous waste plus the list (see Appendix IX to the rule) of 31 organic compounds that are common products of incomplete combustion (PICs) from burning hazardous waste. The total concentration of each nonmetal compound of concern in the waste-derived residue must be compared with the health-based limit. In addition, the concentration of each metal of concern in an extract

from the Toxicity Characteristic Leaching Procedure (TCLP) must not exceed the health-based limits.

The Agency does not have adequate health effects data (e.g., MCLs, RfDs, unit risk values) to establish health-based limits for many compounds listed in Appendix VIII, Part 261. Consequently, we have conservatively established a health-based limit for such compounds based on the 5th lowest percentile value of the health-based values for nonmetal compounds established in Appendix VII to the rule. That value is 0.002 mg/kg. This is the same approach EPA used to establish a RAC for compounds where insufficient health effects data were available to establish a RAC or RsD for the compound.

The rule requires the use of total concentrations of nonmetal compounds rather than extract concentrations for the test of health significance because the purpose of burning toxic nonmetal compounds in these devices should be to destroy the compounds. (Use of total nonmetal concentrations thus serves as a partial check that combustion is being conducted properly.) The health-based limits for the metals in Appendix VIII of the rule are the Toxicity Characteristic (TC) limits (see §261.24) for those metals for which TC limits have been established. To establish health-based limits for the other metals, the Agency applied the same 100 fold dilution factor to leachate concentrations used to establish the TC limits. The Agency has also used this same dilution factor in assessing whether mineral processing wastes satisfy the low hazard prong of the Bevill test. See 54 FR 36630 (Sept. 1, 1989).

To determine if the concentrations of toxic compounds in the waste-derived residues are higher than the health-based limits, owners and operators must obtain and analyze composite samples of waste-derived residues with a composite period not to exceed 24 hours. The sampling approach must be based on (and be consistent with) representative sampling protocols described in SW-846 and must be documented by recordkeeping.

#### D. Recordkeeping

Owners and operators must maintain for a period of three years or until the facility is issued a permit, whichever is longer, records of sampling and analyses of residues to support claims that the waste-derived residue retains the Bevill exclusion.

#### E. Other Considerations

- 1. Generic Determinations. In the October 26, 1989 supplement to the proposed rule, the Agency requested data and information that it could use to support: (1) generic determinations of levels of toxic constituents in normal (i.e., generated without burning/processing hazardous waste) residues; and (2) generic determinations that certain waste-derived residues are not significantly affected by burning/processing hazardous waste, and, thus, remain excluded without the need to make the case-by-case demonstration.
- a. Normal Residues. After review of comments on the 1989 supplemental notice, the Agency concluded that it is not practicable to establish generic concentrations of toxic constituents in normal residues. Commenters noted that there were so many site-specific variables that affect the concentration of toxic constituents in normal residues that this approach was not workable. Variables include the type of industrial furnace, type of fuels burned, and type and source of raw materials used by industrial furnaces. The Agency initially considered establishing generic concentration levels in normal residues to avoid giving an advantage to facilities that use fuels or raw materials with high (i.e., higher than normal for the industry) levels of toxic constituents. Normal residues from such facilities would have high levels of toxic constituents. Thus, waste-derived residues from such facilities could also have high levels of toxic constituents. Consequently, such facilities could burn/process hazardous waste with high levels of toxic constituents without losing the Bevill exclusion of residues. We note that enforcement officials will give priority consideration to those facilities whose residues fail Part 2 (health-based limits) of the test to determine Bevill applicability and rely on Part 1 (comparison with normal residues) to retain the exclusion. Owners and operators must be able to support, at any time, that the nonhazardous waste feedstreams being fed into the device when hazardous waste is fired are the same (or would not decrease the concentrations of toxic constituents in residues) as those fired when the concentrations of toxic constituents in normal residues were determined. If the concentrations of toxic constituents in nonhazardous feedstreams decrease significantly from those concentrations when the normal residue was generated for purposes of establishing normal concentrations of toxic constituents (or if design or operating conditions change such that levels of toxic constituents in normal residue could decrease significantly), then the owner/operator must establish new, lower, concentrations for normal residue.

- b. Excluded Residues. The Agency also concluded that it is not practicable to make generic determinations that certain waste-derived residues are not significantly affected by burning or processing of hazardous waste and, so, remain excluded. This approach is not workable given that the exclusion would have to be conditioned on a number of factors including: (1) the composition, feed rate, and method of feeding the hazardous waste; (2) the type of device; (3) the composition, feed rate, and method of feeding any other fuels; and (3) the composition, feed rate, and method of feeding any raw materials. The data base to support such determinations is not available. Moreover, any such generic exclusion that is necessarily conditioned on so many factors would be of little practical use to the regulated community given the variability of normal operations.
- 2. Burning for Destruction. The case-by-case approach to determine the effect of coburning on residues from Bevill devices focuses on the residues that are actually generated rather than on the purpose for which the hazardous waste is burned. Thus, residues generated from burning hazardous waste in boilers and industrial furnaces for the purpose of destruction<sup>90</sup> are eligible to retain the Bevill exclusion. The Agency's historic approach to the issue of cogenerated residues has been to focus on the character of the residues to ascertain what determines their character the Bevill material or the hazardous waste being burned/processed (see 50 FR 49190 (November 29, 1987)). The statute itself does not directly specify that the purpose of the burning is a relevant criterion, but instead states that certain types of waste are excluded from Subtitle C regulation pending completion of required special studies. Since the Bevill devices would still be engaged in the Bevill activity, and composition of the residues would potentially be unaffected, the Agency sees no absolute bar to allowing Bevill status for such residues.

For example, wastes with low heating value that are not burned for materials recovery or as an ingredient are burned for destruction. We note that such wastes may be burned only by new facilities as incinerators under an operating permit or by those existing facilities operating under interim status that also have certified compliance with the applicable emissions standards.

#### PART FOUR: MISCELLANEOUS PROVISIONS

# I. Regulation of Carbon Regeneration Units

# A. Basis for Regulating Carbon Regenerating Units as Thermal Treatment Units

In today's rule, EPA is clarifying the regulatory status of carbon regeneration <sup>91</sup> units. Since 1980, controlled flame (direct flame) carbon regeneration units which destroy organic contaminants adsorbed onto activated carbon have met the definition of incinerator and were subject to regulation as such, while carbon regeneration nonflame thermal units were treated as exempt reclamation units. Today's rule defines carbon regeneration unit and incinerator (see §260.10) to ensure that both direct flame and nonflame thermal carbon regeneration units are regulated as thermal treatment units under the interim status standards of Part 265, Subpart P, and the permit standards of Part 264, Subpart X.

One commenter expressed concern that the thermal treatment standards of Subpart X were vague. EPA disagrees and points out that Subpart X, Part 264 covers miscellaneous hazardous waste management units that do not or may not fit the description of any of the units covered by other Part 264 regulations. Without Subpart X, these unregulated units could only operate as interim status facilities and could not be fully permitted, thereby preventing the construction of new units or some expansions of existing units. EPA recognized that some types of new units that were not previously allowed to be constructed could reduce risks to human health and the environment from the management of hazardous waste. Promulgation of Subpart X generic permitting standards was intended to allow such construction and flexibility for technical development and innovation and to cover diverse technologies and units. The Subpart X standards specify that health and environmental safety must be a primary concern during the management of hazardous wastes in miscellaneous units. If the need arises, the Agency may develop specific technology standards in the future (see 52 FR 46964, December 10, 1987). Although several commenters supported the application of Part 264, Subpart O incinerator standards to direct flame and nonflame devices, EPA has decided against this since demonstration of conformance with the DRE standards (and the proposed CO/THC standards) may not be achievable or warranted for carbon regeneration units considering the relatively low levels of toxic organic compounds adsorbed onto the activated carbon.

The term "regeneration" includes reactivation of used carbon for reuse.

#### B. Definition of Carbon Regeneration Unit and Revised Definition of Incinerator

Several commenters requested that EPA consider revising the definition of a carbon regeneration unit so that certain units used for air emissions control, wet oxidation, and general recycling, would not be regulated. Activated carbon units used as air emission control devices of gaseous industrial process emissions will not necessarily be regulated because trapped organics in such columns are not hazardous wastes because the gas originally being treated is not a solid waste (it is an uncontained gas<sup>92</sup>), and therefore any condensed organics do not derive from treatment of a hazardous waste. (The nongas residues from these devices could be hazardous wastes if they are listed or if they exhibit a characteristic, however.) However, regeneration or reactivation of carbon used to control air emissions from hazardous waste treatment, storage, or disposal facilities (e.g., under 40 CFR 265 and 265, Subpart II, June 21, 1990, 55 FR 25454) is subject to regulation as a RCRA thermal treatment unit.

We considered whether other units truly are engaged in reclamation, or whether the regeneration of the carbon is just the concluding aspect of the waste treatment process that commenced with the use of activated carbon to adsorb waste contaminants, which are now destroyed in the "regeneration" process (just as rinsing out a container of hazardous waste is a stage in the storage process and does not constitute recycling of the container). Irrespective of whether these units are better classified as waste treatment or recycling units (or whether the units are flame or nonflame devices), we are concerned, as indicated above, that emissions from the regeneration process can pose a serious hazard to public health if not properly controlled, and therefore are clarifying today that they are regulated as thermal treatment units.

We note that this revision also applies to those carbon regeneration units that, while in active service treating wastewater, meet the definition of wastewater treatment units in §260.10. Such units are exempt from RCRA permitting standards while treating wastewater. However, these units are not exempt from RCRA regulation when they are being regenerated because they are not treating wastewater during the regeneration process. Rather, the activated carbon columns themselves are being treated thermally. The thermal regeneration unit is subject to Part 265, Subpart P (existing units) or Part 264, Subpart X (new units).

<sup>92</sup> See 47 FR at 27530 (June 30, 1982) and 54 FR at 50973 (Dec. 11, 1989).

# C. Units in Existence on the Effective Date of the Rule are Eligible for Interim Status

Although certain carbon regeneration units may technically have met either the 1980 or 1985 definitions of incinerator, the Agency believes that there has been legitimate doubt as to these units' regulatory status (which is why the Agency undertook this rulemaking to clarify the status). The units might potentially have been classified as incinerators, thermal treatment units, or perhaps exempt recycling units. It would also have been confusing to interpret the rules in a manner that carbon regeneration units were not all regulated in the same way, given that there functions and activities are roughly identical whether or not the units are direct-fired. In fact, the most natural classification of these units, and the one the Agency intended, is as thermal treatment units. (EPA does not believe that these are recycling units, but rather that regeneration is a continuation of the waste treatment process, that process consisting of removal of pollutants by adsorption followed by their destruction. Nor does the Agency believe that incinerator standards make technical sense for these devices, as noted above.) In addition, few if any of these units have actually been regulated as incinerators in practice.

For these reasons, EPA is finding pursuant to §270.10(e)(2) that there was substantial confusion as to which owners or operators of carbon regeneration units were required to submit a Part A application and that this confusion is attributable to ambiguities in the subtitle C rules. Accordingly, such owners and operators may submit Part A applications by the effective date of today's regulations and be eligible for interim status under Part 265, Subpart P (assuming they meet remaining requirements for interim status eligibility, and the facility is not already subject to interim status for other units).

#### II. Sludge Dryers

In today's rule, the Agency is clarifying the regulatory status of sludge dryers. In particular, the rule adds a definition of "sludge dryer" to \$260.10 and amends the definition of "incinerator" in \$260.10 to specifically exclude sludge dryers.

On November 17, 1980 (45 FR 76074), EPA suspended the applicability of the RCRA permitting requirements (40 CFR Part 122, which is now codified as part 270) and hazardous waste management facility standards (40 CFR Parts 264 and 265) to owners and operators of devices meeting the definition of "wastewater treatment unit" in 40 CFR 260.10 and 270.2.

Since promulgation of this wastewater treatment unit exclusion from RCRA permitting requirements, the Agency has received numerous requests to determine if certain types of units satisfy the definition of "wastewater treatment unit" and, therefore, would not require a RCRA permit. Many of these requests have concerned the regulatory status of thermal treatment units, particularly sludge dryers. Commenters have also requested clarification of the regulatory status of sludges from thermal treatment units. Most of the requests have been from owners and manufacturers of sludge dryers. The Agency believes that approximately 40 sludge dryers are currently being used in the metal finishing industry to dehydrate metal hydroxide sludges (EPA Hazardous Waste F006) generated in the treatment of wastewater.

In response to these inquiries, EPA distributed policy memoranda to the Regional offices explaining that a sludge dryer is included within the scope of the wastewater treatment tank exclusion, provided that it meets the definition of "wastewater treatment unit." (See OSWER Policy Directives 9503.52-1A and 9503.51-1A, available upon request from the RCRA Hotline.) In addition, with respect to the status of the sludges themselves, they are hazardous waste if identified or listed (including by application of the mixture and derived-from rules) and are subject to regulation when removed from the tanks.

Despite the original November 17, 1980 preamble discussion and the policy clarification, the regulatory status of sludge dryers has continued to be unclear. One reason for the confusion is because it is not clear whether a sludge dryer satisfies the third component of the definition of wastewater treatment unit (i.e., whether it meets the definition of a "tank" or "tank system"). The Agency has determined that sludge dryers that are integrally equipped with feed or discharge hoppers that provide for an accumulation of waste satisfy the definition of "tank system." Based on information available to EPA at this time, it appears the most sludge dryers are so equipped. (Those sludge dryers that are not so designed may still be considered tanks, but a case-by-case decision must be made.) The Agency has also determined that other types of equipment not obviously meeting the "tank" definition, such as presses, filters, sumps, and other types of

We note that sludge dryers that are a part of a wastewaster treatment facility that is subject to regulation under either section 402 or 307(b) of the Clean Water Act) and that do not meet the definition of a tank system are subject to RCRA regulation as thermal treatment units, just like sludge dryers that are not a part of a wastewater treatment system.

processing equipment, are covered within the meaning of the term "tank" or "tank system" when used in the context of this exclusion (see OSWER Policy Directive 9503.52-1A).

Another reason that the regulatory status of sludge dryers has been the subject of many questions may be because some sludge dryers technically meet the current definition of an "incinerator," although EPA never intended to regulate direct-flame (or nonflame) sludge dryers as incinerators. When EPA amended the definition of "incinerator" to use physical design criteria rather than a primary purpose test (i.e., purpose of burning) to define an incinerator, it did not intend to bring sludge dryers under regulatory control as incinerators. (See 50 FR 625, January 4, 1985, indicating that the revised definition would not bring large numbers of devices other than incinerators under incinerator standards.) Under the former primary purpose definition, sludge dryers were not incinerators. Although under the 1985 revised definition of incinerator sludge dryers could be classified as incinerators, this was not EPA's intention. The Agency is clarifying this ambiguity by clearly regulating all nonexempt sludge dryers (i.e., those not meeting the definition of "wastewater treatment unit" under today's rule, as discussed below) under the interim status standards of Part 265, Subpart P ("Thermal Treatment"), and the permit standards of Part 264, Subpart X ("Miscellaneous Units"). See 55 FR 17866 (April 27, 1990) for details. Given that such units managing hazardous waste always were subject to some type of regulation, they are not newly eligible for interim status as a result of today's clarification.

Even though as a result of this amendment sludge dryers are potentially subject to regulation under Subpart P of Part 265 and Subpart X of Part 264 as other thermal treatment units, sludge dryers that meet the § 260.10 definitions of "wastewater treatment unit" and "tank" or "tank system" continue to be exempt wastewater treatment units under §§264.1(g)(6) and 265.1(c)(10). The Agency believes that virtually all sludge dryers meet the tank/tank system definition and, therefore, would be exempt when used as part of a wastewater treatment system.

#### A. July 1990 Proposal

To better clarify the regulatory status of sludge dryers, the Agency proposed on July 18, 1990 (55 FR 29280) a definition for "sludge dryer" to clearly distinguish them from other thermal treatment units: Sludge dryer means any enclosed thermal treatment device that is used to dehydrate sludge and that has a maximum total thermal input of 1,500 Btu/lb of sludge treated on a wet-weight basis.

In the same notice, the Agency also proposed to amend the definition of a wastewater treatment unit to say that sludge dryers were the only thermal treatment devices (heretofore) meeting the definition of a wastewater treatment unit that were exempt from regulation.

Today's rule clarifies that sludge dryers meeting the definition of a wastewater treatment unit are exempt from regulation (by promulgating a definition of sludge dryer and revising the definition of incinerator to exclude sludge dryers). EPA also proposed a further clarification that other devices that use heat to treat wastewaters were not to be considered eligible for the wastewater treatment tank exemption. The Agency indicated, without discussion, that it had not intended for such units to be eligible for the exemption and that the proposal was a simple clarification which reflected common understanding within the Agency and the regulated community.

Commenters disagreed with this assessment of the regulations, and the Agency has since studied the issue in more depth. It appears that the Agency was mistaken in its assessment both of the current intended scope of the rule and of common understanding of what the rule covers. With respect to such devices as evaporators and steam strippers used in wastewater treatment, the Agency has in fact traditionally regarded such units as eligible for the wastewater treatment exemption. See 55 FR at 25467 (June 21, 1990). Commenters likewise indicated their understanding that current rules exempt such devices.

Given the narrow scope of the proposal, the clear indication that any change would not be a clarification of existing rules (as indicated) but rather a potentially far-reaching alteration, and the absence of any discussion (or study) of whether a substantive change in regulatory status of these devices is warranted, EPA cannot go forward. Consequently, we are not adopting any other part of the definition of wastewater treatment unit discussed in the 1990 notice.

#### B. Summary of Public Comments

EPA received comments regarding the status of sludge dryers in response to the April 27, 1990 BIF notice and the July 18, 1990 notice discussed above.

Many of the commenters to these notices supported the inclusion of sludge dryers in the wastewater treatment unit (WWTU) definition. The commenters, however, requested clarification on whether units similar to sludge dryers (e.g., evaporators) would

also be eligible for the WWTU exclusion. As discussed above, other devices using heat that meet the definition of wastewater treatment unit would continue to be exempt from RCRA regulation (except, of course, an incinerator, boiler, or industrial furnace burning hazardous waste).

Eleven commenters to these proposals stated that the maximum 1,500 Btu/lb thermal input requirement in the sludge dryer definition is too low. Citing low thermal efficiencies (especially for indirect-fired dryers), these commenters recommended thermal input requirements ranging from 1,700 to 3,300 Btu/lb.

After consideration of the commenters' concerns and further review of the technical background information on the thermal input limit, the Agency is today revising the thermal input limit to 2,500 Btu/lb wet sludge. The Agency believes that depending on the nature of the treatment system, the thermal input to a bona fide sludge dryer (i.e., a device that is not an incinerator) can be as high as 2,500 Btu/lb.

Several commenters also requested that EPA clarify that the total thermal input limit was not to include the heating value of the sludge itself given that a number of sludges that are dried have as-fired heating values of 1,000 to 2,700 Btu/lb. The Agency agrees. The final rule explicitly excludes the heating value of the sludge from the 2,500 Btu/lb limit on thermal input. With this clarification, however, we note that the primary purpose test --dehydration -- is the primary distinction between a sludge dryer and an incinerator. This is because a sludge incinerator can readily meet the thermal heat input limit of 2,500 Btu/lb when the heating value of the sludge itself is not included. However, the primary purpose of a sludge dryer is dehydration while the primary purpose of an incinerator is volume reduction to produce an ash residue. Thus, we believe that the definition in today's rule adequately distinguishes between sludge dryers and incinerators. Nevertheless, it should be noted that any person claiming the wastewater treatment unit exemption for a sludge dryer must have documentation to support that the primary purpose of the device is to dehydrate sludge, not to destroy sludge to produce an ash residue.

The Agency received many responses to its request for comments on whether it is necessary to specify a minimum percent volume reduction in the definition of a sludge dryer. Although one commenter stated that a percent volume reduction should be specified in the sludge dryer definition, twelve of the commenters stated that such a requirement would be arbitrary, confusing, unworkable, and costly to enforce. Two of the commenters stated that a minimum percent weight reduction would be more appropriate. In today's

rule, the Agency has decided not to specify a minimum percent volume (or weight) reduction in the definition of a sludge dryer. The Agency believes that such a specification would be difficult to support and would not be needed to distinguish sludge dryers from incinerators.

Several commenters stated that the Agency should address emissions of volatile organics from units such as sludge dryers. In addition, two commenters recommend a 1,000 Btu/lb thermal input limit for the device to control volatile emissions from sludge dryers. EPA recognizes the need to address volatile emissions from sludge dryers and intends to evaluate alternatives for regulating these units at a later date. However, because this rule simply clarifies that EPA intended for sludge dryers that meet the definition of a wastewater treatment unit to be exempt from the RCRA rules, it would be inappropriate to address volatile organic emissions at this time. Nonetheless, sludge dryers that do not meet the definition of a wastewater treatment unit (e.g., sludge dryers that are not a part of a wastewater treatment facility that is subject to regulation under either section 402 or 307(b) of the Clean Water Act) are subject to regulation as thermal treatment units under Subpart X of Part 264. Under those standards, the Agency may apply controls on volatile organic (and other) emissions as necessary to protect human health and the environment.

After considering comments on the proposed sludge dryer definition, EPA is today promulgating the following definitions:

Sludge dryer means any enclosed thermal treatment device that is used to dehydrate sludge and that has a maximum total thermal input, excluding the heating value of the sludge itself, of 2,500 Btu/lb of sludge treated on a wet-weight basis.

Incinerator means any enclosed device that: (1) uses controlled flame combustion and neither meets the criteria for classification as a boiler, carbon regeneration unit, or a sludge dryer, nor is listed as an industrial furnace; or (2) meets the definition of infrared incinerator or plasma arc incinerator.

#### III. Classification of Coke and By-Product Coal Tar

#### A. AISI Petition

The American Iron and Steel Institute (AISI) petitioned EPA with respect to the practice of recycling tar decanter sludge by the following means:

- 1. Applying the sludge to coal prior to or just after charging the coal into the coke oven; and,
- 2. Combining the sludge with coal tar prior to its being sold.

The coke and the coal tar are often used as fuel and so have been classified as solid wastes and hazardous wastes since they are fuels produced or otherwise containing a hazardous waste -- EPA Hazardous Waste No. K087, tar decanter sludge. See §261.2(c)(2)(i)(B). These hazardous waste fuels have been exempt from regulation under § 261.6(a)(3)(vii) and 50 FR 49170-171 (November 29, 1985). The AISI has requested that EPA not classify such coke or coal tar as solid wastes. AISI submits that recycling the decanter sludge in this manner does not significantly affect the concentration of toxic metal and organic constituents of the coke or coal tar. EPA has indicated that waste-derived fuels could be classified as products under such circumstances, "since the more waste-derived fuels from a process are like products from the same process produced by virgin materials, the less likely EPA is to classify the waste-derived fuel as a waste." 50 FR 49169 (Nov. 29, 1985). To support its request, the AISI submitted data on the metals and organic constituents in coke, coal tar, and tar decanter sludge both with and without sludge recycling. The data and the Agency's response are discussed below.

# B. Process Description

Coke used for making iron is manufactured through the destructive distillation of coal in ovens. A typical oven holds approximately 13 tons of coal which is heated to a temperature of about 2000°F. Generally 20 to 100 ovens are located adjacent to each other in a "coke oven battery." The destructive distillation or "coking" process takes about 15-18 hours. During that time period, about 20-35 percent of the coal is converted to coke oven gas (COG) consisting of water vapor, tar, light oils, heavy hydrocarbons, and other chemical compounds. The COG is collected from the top of the coke oven and, in most cases, sent to the by-product plant via the coke battery main. The COG is then cleaned by removing wastes and by-products prior to being burned, generally in the coke oven underfiring system. As a first step in the COG cleaning process, the coal tars, consisting of heavy hydrocarbons, are condensed from the gas. In addition, most of the particulate that escapes from the ovens is collected in the tar. This particulate is believed to consist principally of coal fines. The particulate or solids are then removed from the tar in the tar decanter. The coal tar is then burned as fuel or sold for use in various products such as

roofing cement. The sludge has been listed as EPA Hazardous Waste No. K087 and is disposed of or recycled either by mixing with coal prior to being charged to the coke oven or mixing with coal tar after physical processing (grinding) prior to sale.

Approximately 8-12 gallons of tar are produced per ton of coke. In addition, approximately one pound of tar decanter sludge is produced for every 40 pounds of tar produced.

# C. Basis for Approval of the AISI Petition

The AISI submitted data from metal and organic chemical analyses for the coke, coal tar, and tar decanter sludge from four plants. The Agency reviewed these results and determined the following:

- 1. The recycling of tar decanter sludge by application to the coal charge does not appear to have a significant effect on the chemical composition of coke;
- 2. The organic chemical composition of the tar decanter sludge does not appear to be significantly different from the coal tar, and,
- 3. The concentration of one metal, lead, in the sludge appears to be slightly higher than in the coal tar. However, the increase does not appear to be statistically significant due to the high variability of the concentration values.

Based on the above and the fact that there is such a small quantity of sludge relative to the quantity of coke and coal tar produced by the coking process, EPA believes that sludge recycling, as described here, does not significantly affect the concentration of toxic metals and organic constituents in coal tar or coke. Furthermore, coke, coal tar, and the decanter tank tar sludge are similar materials formed in a single process and contain the same contaminants. In this circumstance, when the coke and the decanter tank tar sludge are very nearly the identical substance and, moreover, come from a single process, the Agency is warranted in exercising its discretion to determine that this management of the sludge is "not part of the waste disposal problem", and hence that the coke product is no longer a RCRA solid waste. American Mining Congress v. EPA, 907 F. 2d 1179, 1186 (D.C. Cir. 1990). Therefore, in today's rule, EPA is classifying such coke and coal tar as products, not wastes. As a result, the coke and coal tar will be excluded under 40 CFR 261.4 from the definition of solid waste and not subject to RCRA hazardous waste management regulations when used as a fuel. A necessary corollary to this action is also to exclude the coking process from regulation when K087 is used as an ingredient to produce coke. Given that K087 is for practical purposes just like other materials used to produce coke and comes from the same process as these other materials, it would be anomalous to assert RCRA control over the coking process. Again, this form of sludge management — which is the same as raw material management — does not appear to EPA to be part of the waste disposal problem.<sup>94</sup> (In addition, coke ovens are subject to a special regulatory regime under amended section 112(i)(8) of the Clean Air Act, and RCRA regulation of this particular practice could disrupt the Clean Air Act regulatory scheme. Thus, the Agency views RCRA regulation of this practice as inappropriate in any case.)

This exemption applies only to the waste-derived fuels and only when derived from tar decanter sludge, K087. Thus the tar decanter sludge, K087, is subject to full RCRA regulation prior to recycling. In addition, the exemption does not extend to coke or coal tar produced from hazardous waste (e.g., spent solvents) other than tar decanter sludge, EPA Hazardous Waste K087.

#### IV. Regulation of Landfill Gas

In the November 29, 1985 final rules regulating hazardous waste burned for energy recovery, the Agency indicated that gas recovered from hazardous waste landfills that is burned for energy recovery in boilers or industrial furnaces is not regulated under the waste-as-fuel rules. 50 FR 49171. EPA took this action in order to study further the extent to which there might be jurisdictional limits on the Agency's authority under section 3004(n) of RCRA to regulate gaseous emissions from hazardous waste. *Id.* In today's rule, we are amending this language slightly by indicating that the exemption also applies to gas recovered from solid waste landfills. Therefore, gas recovered from a solid waste landfill that exhibits a hazardous characteristic would also be exempt from today's rule when burned for energy recovery in a boiler and industrial furnace.

In addition, the Agency solicited comment, in the May 6, 1987 proposed rule, on whether the hydrocarbon phase of the condensate removed from recovered gas should also be exempt from regulation when burned as fuel (52 FR 17021). Two commenters responded that the condensate contains chemical constituents similar to fossil fuels such as kerosene or gasoline and that the handling and burning of the gas condensate poses no significant hazard to human health. The commenters encouraged the Agency not to regulate

The Agency is not aware of any other hazardous wastes that are burned in coke ovens as an ingredient that are just like other materials used to produce coke. If such materials are used, the Agency would encourage the industry to provide the necessary information in order to determine whether the exclusion should be modified.

the hydrocarbon phase of the landfill gas condensate unless the hydrocarbons exhibit a Subtitle C characteristic of a hazardous waste. However, data on condensate composition provided by one respondent was vague and represented only one source of condensate. Absent adequate data, EPA is not promulgating an exemption from regulation of the hydrocarbon phase of the landfill gas condensate at this time. Facilities that wish to burn a landfill gas condensate may consider whether they are eligible for the small quantity burner exemption promulgated in this rule.

#### V. Definitions of Infrared and Plasma Arc Incinerators

Today's rule establishes definitions for infrared and plasma arc incinerators and revises the definition of incinerator to explicitly include these devices. As discussed in the April 27, 1990 proposed amendments to the incinerator standards (55 FR at 17869-70), EPA is clarifying that these devices are incinerators rather than (other) thermal treatment units subject to regulation under Subpart X of Part 264 (or Subpart P of Part 265 for interim status units) because: (1) although these devices use nonflame sources of thermal energy to treat waste in the primary chamber, they invariably employ controlled flame afterburners to combust hydrocarbons driven off by the primary process (and, thus, they meet the definition of an "incinerator" under §260.10); and (2) the incinerator standards are workable and protective for these units.

We note that today's action merely clarifies the regulatory status of these devices. It does not subject them to regulation for the first time; they have been regulated since 1980. Thus, interim status is not reopened for these devices.

# PART FIVE: ADMINISTRATIVE, ECONOMIC, AND ENVIRONMENTAL IMPACTS, AND LIST OF SUBJECTS

#### I. State Authority

#### A. Applicability of Rules in Authorized States

Under Section 3006 of RCRA, EPA may authorize qualified States to administer and enforce the RCRA program within the State. (See 40 CFR Part 271 for the standards and requirements for authorization.) Following authorization, EPA retains enforcement authority under Sections 3008, 7003 and 3013 of RCRA, although authorized States have primary enforcement responsibility.

Prior to the Hazardous and Solid Waste Amendments of 1984 (HSWA), a State with final authorization administered its hazardous waste program entirely in lieu of EPA

administering the Federal program in that State. The Federal requirements no longer applied in the authorized State, and EPA could not issue permits for any facilities in the State which the State was authorized to permit. When new, more stringent Federal requirements were promulgated or enacted, the State was obliged to enact equivalent authority within specified time frames. New Federal requirements did not take effect in an authorized State until the State adopted the requirements as State law.

In contrast, under Section 3006(g) of RCRA, 42 U.S.C. 6926(g), new requirements and prohibitions imposed by HSWA take effect in authorized States at the same time that they take effect in nonauthorized States. EPA is directed to carry out those requirements and prohibitions in authorized States, including the issuance of permits, until the State is granted authorization to do so. While States must still adopt HSWA-related provisions as State law to achieve or retain final authorization, the HSWA applies in authorized States in the interim.

The majority of today's rule is promulgated pursuant to Section 3004(q) of RCRA, a provision added by HSWA. (The provisions that are not promulgated pursuant to HSWA are the provisions for sludge dryers, carbon regeneration units, infrared incinerators, and plasma are incinerators.) Therefore, the Agency is adding the requirements (except the non-HSWA provisions) to Table 1 in §271.1(j) which identifies the Federal program requirements that are promulgated pursuant to HSWA and that take effect in all States, regardless of their authorization status. States may apply for either interim or final authorization for the HSWA provisions identified in Table 1, as discussed in the following section of this preamble.

#### B. Effect on State Authorizations

As noted above, EPA will implement the majority of the provisions of today's rule in authorized States until they modify their programs to adopt these rules and the modification is approved by EPA. Because these provisions of the rule are promulgated pursuant to HSWA, a State submitting a program modification may apply to receive either interim or final authorization under Section 3006(g)(2) or 3006(b), respectively, for these provisions on the basis of requirements that are substantially equivalent or equivalent to EPA's. The procedures and schedule for State program modifications for either interim or final authorization are described in 40 CFR 271.21. It should be noted that all HSWA interim authorizations will expire January 1, 1993. (See §271.24(c).)

The provisions of today's rule that are not promulgated pursuant to HSWA -provisions for sludge dryers, carbon regeneration units, infrared incinerators, and plasma
are incinerators -- are not effective in authorized States. Thus, these requirements will be
applicable only in those States that do not have final authorization. In authorized States, the
requirements will not be applicable until the State revises its program to adopt equivalent
requirements under State law.

40 CFR 271.21(e)(2) requires that States that have final authorization must modify their programs to reflect Federal program changes, and must subsequently submit the modifications to EPA for approval. The deadline by which the State must modify its program to adopt the HSWA portion of today's rule is July 1, 1993 if a statutory change is not needed, or July 1, 1994 if a statutory change is needed. The deadline by which the State must modify its program to adopt the non-HSWA portion of today's rule is July 1, 1992 if a statutory change in not needed, or July 1, 1993 if a statutory change is needed. These deadlines can be extended in certain cases (40 CFR 271.21(e)(3)). Once EPA approves the modification, the State requirements become Subtitle C RCRA requirements.

States with authorized RCRA programs may already have requirements similar to those in today's rule. These State regulations have not been assessed against the Federal regulations being promulgated today to determine whether they meet the tests for authorization. Thus, a State is not authorized to implement these requirements in lieu of EPA until the State program modification is approved. Of course, States with existing standards may continue to administer and enforce their standards as a matter of State law.

In implementing the Federal program for the HSWA portion of today's rule, EPA will work with States under cooperative agreements to minimize duplication of efforts. In many cases, EPA will be able to defer to the States in their efforts to implement their programs, rather than take separate actions under Federal authority.

States that submit their official applications for final authorization less than 12 months after the effective date of these standards are not required to include standards equivalent to these standards in their application. However, the State must modify its program by the deadlines set forth in §271.21(e). States that submit official applications for final authorization 12 months after the effective date of these standards must include standards equivalent to these standards in their application. 40 CFR 271.3 sets forth the requirements a State must meet when submitting its final authorization application.

#### II. Regulatory Impacts

#### A. Cost Analysis

1. Background. Prior to publication of the proposed regulations in May 1987, the Agency examined the projected compliance costs, economic impacts, and risk reductions associated with the proposed rules. This effort consisted of a detailed examination of the pre-proposal draft as it was drafted in mid-1986 and a supplement prepared in late 1986<sup>95</sup> that examined several changes in tax policy and regulatory approach that occurred after the first analysis was completed.<sup>96</sup>

The analyses estimated that of the approximately 1,000 BIFs identified as firing hazardous wastes, approximately 20 percent were likely to discontinue burning hazardous wastes because of the rules, 60 percent would burn small amounts of waste and would qualify for the small quantity burner exemption (SQBE), and the remaining 15 percent would obtain full permits. Because the final 15 percent of devices represent large facilities, however, the impact on the total quantity of waste burned would be small. For example, under the "base case" scenario, although 20 percent of the devices would discontinue burning hazardous wastes and a number of other devices would reduce the quantity of hazardous waste they combust in order to qualify for the SQBE, only 3 percent of the quantity of waste combusted in the absence of regulations would be diverted to other devices. The mid-1986 analysis estimated that under this scenario, the aggregate after-tax cost of compliance to individual firms would be \$5.2 million per year and that the before-tax social cost would be \$8.2 million per year. Under other sets of assumptions (i.e., other scenarios), these costs were likely to be higher, but in all cases were estimated to be less than \$100 million per year.

Based on these analyses, the Agency concluded that the total social costs, impact on market competition, and the impact on small businesses were such that the proposed regulations did not constitute a major rule, and that a formal Regulatory Impact Analysis as described in Executive Order 12291 was not required.

U.S. EPA, "Regulatory Analysis for Waste-As-Fuel Technical Standards", Draft Report, October 1986.

U.S. EPA, "Effects of Recent Changes on the Estimated Costs and Benefits of the Proposed Waste As Fuel Technical Standards", January 1987.

A number of comments on the economic analysis were received from affected businesses and other groups. Most of these commenters contended that the cost of compliance had been underestimated by the Agency. Based on these comments, as well as changes made in the final regulation compared to the proposed requirements, the Agency has reexamined and updated the earlier analyses.

2. Revised Cost Analysis. As indicated earlier, there have been a number of changes made in the regulations that are expected to increase the cost of compliance. In addition, the Federal tax code was changed in late 1986, the cost of goods and services to the economy as a whole has increased due to inflation, and the estimated cost of specific requirements associated with the BIF regulations have been reexamined. The new analysis focused on assessing the impact of changes in compliance costs on typical facilities, and did not reexamine the impact of these changes on the selection of regulatory options by individual facilities. In addition, no effort was made to explicitly examine the impact of the final rules on the economic competitiveness of individual firms or industries, nor on the reduction in public health risks.

The primary changes that have occurred in the regulations subsequent to proposal have been revised requirements for continuous emission monitoring of CO and HC; addition of the PM standard, interim status compliance procedures, and limits on emissions of several additional metals and Cl<sub>2</sub>; and increases in recordkeeping, sampling, and analysis requirements. The impact of these changes plus the impact of tax code changes and inflation on the before- and after-tax costs of the BIF regulations are summarized in Table 1. When combined with the original "base case" cost estimates prepared in 1986, the revised cost estimate for the promulgated rule is \$15.2 million per year before taxes and \$10.3 million per year after-taxes.

The increased cost for CO and HC monitoring reflects the costs for installation of a more comprehensive CO monitoring system than was originally estimated and the cost of installing HC monitors on an estimated 20 devices (primarily cement kilns) that will operate under the Tier II CO and HC limits. The zero cost increase associated with the PM emission standard reflects the expectation that BIFs complying with the metals standards will achieve the 0.08 gr/dscf standard, and that most existing industrial furnaces and some boilers are already subject to this emission level (or a more stringent level) as the result of State Implementation Plans or New Source Performance Standards. As a result, no incremental increase for compliance with the PM emission limit is projected.

The additional costs for interim status compliance reflects the increase in annualized costs (over a 10 year period) for preparation of the precompliance and compliance certification packages (including compliance testing) by approximately 150 BIFs. The additional cost for the Cl<sub>2</sub> standard is based on the incremental cost of analysis for Cl<sub>2</sub> beyond that already required to determine HCl emissions.

The increase in annual recordkeeping, sampling, and analysis costs reflects a reassessment of the estimated costs in the 1986 analysis. These increased costs reflect a before-tax increase of approximately \$2.4 million for recordkeeping and \$0.6 million for sampling and analysis.

The impact of the 1986 tax code changes was to reduce the marginal tax rate imposed on before-tax profits and, thus, has the affect of increasing the impact of compliance costs on after-tax profits. As a result, the change in the 1986 tax code is to increase the after-tax cost of the regulations by an estimated \$0.6 million per year. The increase in costs due to inflation reflects an estimated increase in compliance cost of 20 percent between the time of the initial analysis (based on 1985 dollars) and 1990.

TABLE 1

Cost Element	Before Taxes	After Taxes	Note
CO and HC Monitoring	1,930,000	1,200,000	1
PM Standard	. 0	0	2
Interim Status Compliance	980,000	590,000	3
Cl <sub>2</sub> Standards	30,000	20,000	4
Recordkeeping/Sampling & Analysis	3,050,000	1,700,000	5
Tax Code Changes	0	600,000	6
Inflation	1.640,000	980,000	7
	7,630,000	5,090,000	

#### Notes:

- 1. Based on installing 20 CO monitors using capital and O&M costs from the revised ICR.
- 2. No incremental costs because BIFs already meet standard by meeting metals limits and existing SIP and NSPS limits.
- 3. Assumes all not small quantity burner BIFs submit precompliance and compliance certification packages, 50% of BIFs submit a revised certification of precompliance, and 75% of compliance test can be used in lieu of the trial burn to obtain an operating permit, thus reducing the cost of the Part B permit.
- 4. Assumes all BIFs complying with emissions limits (and not Tier I feed rate limits) conduct Cl2 testing during compliance certification and trial burn tests (\$165/sample).
- 5. Increases waste sampling and analysis costs over those estimated at proposal for all non-small quantity burners by \$300/month. Provides an additional 16 hours per month for all non-small quantity burners and 2 hours per month for small quantity burners for additional recordkeeping.
- 6. The 1986 revisions to the Federal tax code reduced the Federal marginal tax rate (MTR) from 48% to 34%. The 1986 analysis assumed a MTR of 50% (48% Federal plus 2% State). The revised analysis assumes a MTR of 40% (34% Federal plus 6% State).
- 7. Adjustment for 20% inflation between 1985 and 1990 (\$8.2 million before tax cost estimate in 1985 dollars, adjusted to after-tax basis assuming a marginal tax rate of 40%.

#### B. Regulatory Flexibility Act

The Regulatory Flexibility Act (RFA) requires Federal regulatory agencies to evaluate the impacts of regulations on small entities. The RFA requires an initial screening analysis to determine whether the proposed rule will have a significant impact on a substantial number of small businesses. As indicated at proposal (52 FR 17030), the Agency estimates that a substantial number of small entities will not be significantly impacted by the rule. Although the Agency estimates that changes to the rule since proposal and re-evaluation of some cost estimates made during the initial impact analysis will result in a higher cost to the regulated industry, the Agency continues to believe that a substantial number of small entities will not be significantly impacted by the rule.

#### C. Paperwork Reduction Act

The information collection requirements in this rule have been submitted for approval to the Office of Management and Budget (OMB) under the *Paperwork Reduction* Act 44 U.S.C. 3501 et seq.

#### III. List of Subjects

Administrative practices and procedures, Confidential business information, Hazardous materials transportation, Hazardous waste, Indian lands, Insurance, Intergovernmental relations, Packaging and containers, Penalties, Recycling, Reporting and recordkeeping requirements, Security measures, Security bonds, Water pollution control, Water supply.

Dated:

12-31-90

F. Henry Habicht, II

Deputy Administrator AND ACTING ADMINISTRATOR

# PART 260-HAZARDOUS WASTE MANAGEMENT SYSTEM: GENERAL

- I. In Part 260:
- 1. The authority citation for Part 260 continues to read as follows:

Authority: 42 U.S.C. 6905, 6912(a), 6921 through 6927, 6930, 6934, 6935, 6937, 6938, 6939, and 6974.

2. Section 260.10 is amended by: (1) revising the introductory sentence; (2) revising the definition of "incinerator"; (3) revising the definition of "industrial furnace" by revising the introductory text and redesignating paragraph (12) as (13) and by adding new paragraph (12); and (4) adding, in alphabetical order, definitions for "carbon regeneration unit," infrared incinerator", "plasma are incinerator" and "sludge dryer" to read as follows:

#### § 260.10 Definitions.

When used in Parts 260 through 266 and 268 of this chapter, the following terms have the meanings given below:

Carbon regeneration unit means any enclosed thermal treatment device used to regenerate spent activated carbon.

Incinerator means any enclosed device that:

- (1) Uses controlled flame combustion and neither meets the criteria for classification as a boiler, sludge dryer, or carbon regeneration unit, nor is listed as an industrial furnace; or
  - (2) Meets the definition of infrared incinerator or plasma arc incinerator.

Industrial furnace means any of the following enclosed devices that are integral components of manufacturing processes and that use thermal treatment to accomplish recovery of materials or energy:

(12) Halogen acid furnaces (HAFs) for the production of acid from halogenated hazardous waste generated by chemical production facilities where the furnace is located on the site of a chemical production facility, the acid product has a halogen acid content of at least 3%, the acid product is used in a manufacturing process, and, except for hazardous waste burned as fuel, hazardous waste fed to the furnace has a minimum halogen content of 20% as-generated.

\* \* \*

Infrared incinerator means any enclosed device that uses electric powered resistance heaters as a source of radiant heat and which is not listed as an industrial furnace.

\* \* \*

Plasma arc incinerator means any enclosed device using a high intensity electrical discharge or arc as a source of heat and which is not listed as an industrial furnace.

\* \* \*

Sludge dryer means any enclosed thermal treatment device that is used to dehydrate sludge and that has a maximum total thermal input, excluding the heating value of the sludge itself, of 2,500 Btu/lb of sludge treated on a wet-weight basis.

• •

- 3. Paragraph (a) of § 260.11 is amended by adding the following references in alphabetical order:
- § 260.11 References.
  - (a) \* \* \*
- U.S. EPA, Guideline on Air Quality Models (Revised) (1986) and Supplement A (1987), available from the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161, (703) 487-4600. The document numbers are: PB86-245-248 (Guideline) and PB88-150-958 (Supplement A).
- U.S. EPA, Methods Manual for Compliance with the BIF Regulations, December 1990, available from the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161, (703) 487-4600. The document number is PB91-120-006.
- U. S. EPA, <u>Screening Procedures for Estimating Air Quality Impact of Stationary Sources</u>, August 1988, Available from the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161, (703) 487-4600. The document number is PB89-159-396.

. . . . .

#### PART 261--IDENTIFICATION AND LISTING OF HAZARDOUS WASTE

#### II. In Part 261:

1. The authority citation for Part 261 continues to read as follows:

Authority: 42 U.S.C. 6905, 6912(a), 6921, 6922, and 6938.

2. Section 261.2 is amended by redesignating paragraph (d)(2) as (d)(3) and adding new paragraph (d)(2) to read as follows:

§261.2 Definition of solid waste.

\* \* \* \* \*

- (d) \* \* \*
- (2) Secondary materials fed to a halogen acid furnace that exhibit a characteristic of a hazardous waste or are listed as a hazardous waste as defined in subparts C or D of this part.
- 3. Section 261.4 is amended by adding paragraph (a)(10) and revising paragraphs (b)(4), the first sentence of (b)(7), and (b)(8) to read as follows:

## § 261.4 Exclusions.

- (a) \* \* \*
- (10) When used as a fuel, coke and coal tar from the iron and steel industry that contains or is produced from decanter tank tar sludge, EPA Hazardous Waste K087. The process of producing coke and coal tar from such decanter tank tar sludge in a coke oven is likewise excluded from regulation.
  - (b) \* \* \*
- (4) Fly ash waste, bottom ash waste, slag waste, and flue gas emission control waste, generated primarily from the combustion of coal or other fossil fuels, except as provided by §266.112 of this chapter for facilities that burn or process hazardous waste.
- (7) Solid waste from the extraction, beneficiation, and processing of ores and minerals (including coal, phosphate rock and overburden from the mining of uranium ore), except as provided by §266.112 of this chapter for facilities that burn or process hazardous waste.
- (8) Cement kiln dust waste, except as provided by §266.112 of this chapter for facilities that burn or process hazardous waste.
- 4. Section 261.6 is amended by deleting paragraph (a)(3)(vii) and renumbering paragraphs (a)(3)(viii) and (ix) as (a)(3)(vii) respectively.

## PART 264--STANDARDS FOR OWNERS AND OPERATORS OF HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES

#### III. In Part 264:

1. The authority citation for Part 264 continues to read as follows:

Authority: 42 U.S.C. 6905, 6912(a), 6924, and 6925.

2. § 264.112 is amended by revising paragraph (d)(1) to read as follows:

## § 264.112 Closure of plan; amendment of plan.

(d) Notification of partial closure and final closure. (1) The owner or operator must notify the Regional Administrator in writing at least 60 days prior to the date on which he expects to begin closure of a surface impoundment, waste pile, land treatment or landfill unit, or final closure of a facility with such a unit. The owner or operator must notify the Regional Administrator in writing at least 45 days prior to the date on which he expects to begin final closure of a facility with only treatment or storage tanks, container storage, or incinerator units to be closed. The owner or operator must notify the Regional Administrator in writing at least 45 days prior to the date on which he expects to begin

3. § 264.340 is amended by revising paragraph (a) to read as follows:

partial or final closure of a boiler or industrial furnace, whichever is earlier.

## § 264.340 Applicability.

(a) The regulations of this subpart apply to owners and operators of hazardous waste incinerators (as defined in § 260.10 of this chapter), except as § 264.1 provides otherwise.

## PART 265--INTERIM STATUS STANDARDS FOR OWNERS AND OPERATORS OF HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES

IV. In Part 265:

1. The authority citation for Part 265 continues to read as follows:

Authority: 42 U.S.C. 6905, 6912(a), 6924, 6925, and 6935.

2 § 265.112 is amended by revising paragraphs (a), (d)(1), and (d)(2) to read as follows:

#### § 265.112 Closure plan; amendment of plan.

(a) Written plan. By May 19, 1981, or by six months after the effective date of the rule that first subjects a facility to provisions of this section, the owner or operator of a hazardous waste management facility must have a written closure plan. Until final closure is completed and certified in accordance with §265.115, a copy of the most current plan must be furnished to the Regional Administrator upon request, including request by mail. In addition, for facilities without approved plans, it must also be provided during site inspections, on the day of inspection, to any officer, employee, or representative of the Agency who is duly designated by the Administrator.

4

- (d) Notification of partial closure and final closure. (1) The owner or operator must submit the closure plan to the Regional Administrator at least 180 days prior to the date on which he expects to begin closure of the first surface impoundment, waste pile, land treatment, or landfill unit, or final closure if it involves such a unit, whichever is earlier. The owner or operator must submit the closure plan to the Regional Administrator at least 45 days prior to the date on which he expects to begin partial or final closure of a boiler or industrial furnace. The owner or operator must submit the closure plan to the Regional Administrator at least 45 days prior to the date on which he expects to begin final closure of a facility with only tanks, container storage, or incinerator units. Owners or operators with approved closure plans must notify the Regional Administrator in writing at least 60 days prior to the date on which he expects to begin closure of a surface impoundment, waste pile, landfill, or land treatment unit, or final closure of a facility involving such a unit. Owners or operators with approved closure plans must notify the Regional Administrator in writing at least 45 days prior to the date on which he expects to begin partial or final closure of a boiler or industrial furnace. Owners or operators with approved closure plans must notify the Regional Administrator in writing at least 45 days prior to the date on which he expects to begin final closure of a facility with only tanks, container storage, or incinerator units.
- (2) Except for boilers and industrial furnaces that operate under interim status as specified by §266.103(c)(7)(i)(B) or (C), the date when he "expects to begin closure" must be either within 30 days after the date on which any hazardous waste management unit receives the known final volume of hazardous wastes, or, if there is a reasonable possibility that the hazardous waste management unit will receive additional hazardous wastes, no later than one year after the date on which the unit received the most recent volume of hazardous waste. If the owner or operator of a hazardous waste management unit can demonstrate to the Regional Administrator that the hazardous waste management unit or facility has the capacity to receive additional hazardous wastes and he has taken, and will continue to take, all steps to prevent threats to human health and the environment, including compliance with all interim status requirements, the Regional Administrator may approve an extension to this one-year limit. For boilers and industrial furnaces that operate under interim status as specified by § 266.103(c)(7)(i)(B) or (C), the date when he "expects to begin closure" must be within 30 days after failure to submit a complete certification of compliance by the applicable deadline under § 266.103(c)(7)(i)(B) or (C).

3 §265.113 is amended by revising paragraphs (a) and (b) to read as follows:

#### § 265.113 Closure; time allowed for closure.

(a) Within 90 days after receiving the final volume of hazardous wastes at a hazardous waste management unit or facility, or within 90 days after approval of the closure plan, whichever is later, or, for a boiler or industrial furnace that does not submit a complete certification of compliance by the applicable deadline under §266.103(c)(7)(i)(B) or (C), within 90 days after the applicable deadline, the owner or operator must treat, remove from the unit or facility or dispose of on-site, all hazardous wastes in accordance with the approved closure plan. The Regional Administrator may approve a longer period if the owner or operator demonstrates that:

\* \* \*

- (b) The owner or operator must complete partial and final closure activities in accordance with the approved closure plan and within 180 days after receiving the final volume of hazardous wastes at the hazardous waste management unit or facility, or 180 days after approval of the closure plan, if that is later, or, for a boiler or industrial furnace that does not submit a complete certification of compliance by the applicable deadline under § 266.103(c)(7)(i)(B) or (C), within 180 days after the applicable deadline. The Regional Administrator may approve an extension to the closure period if the owner or operator demonstrates that:
  - 4. § 265.340 is amended by revising paragraph (a) to read as follows:

## § 265.340 Applicability.

(a) The regulations of this subpart apply to owners and operators of hazardous waste incinerators (as defined in § 260.10 of this chapter), except as § 265.1 provides otherwise.

# PART 266--STANDARDS FOR THE MANAGEMENT OF SPECIFIC HAZARDOUS WASTES AND SPECIFIC TYPES OF HAZARDOUS WASTE MANAGEMENT FACILITIES

#### V. In Part 266:

1. The authority citation for Part 266 continues to read as follows:

Authority: Secs. 1006, 2002(a), 3004, and 3014 of the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976, as amended (42 U.S.C. 6905, 6912(a), 6924, and 6934).

2. Subpart D is hereby removed and reserved and Subpart H is added to read as follows:

#### Subpart H -- Hazardous Waste Burned in Boilers and Industrial Furnaces

Sec.	
§ 266.100	Applicability.
§ 266.101	Management prior to burning.
§ 266.102	Permit standards for burners.
§ 266.103	Interim status standards for burners.
§ 266.104	Standards to control organic emissions.
§ 266.105	Standards to control particulate matter.
§ 266.106	Standards to control metals emissions.
§ 266.107	Standards to control hydrogen chloride (HCl) and chlorine gas (Cl <sub>2</sub> )
	emissions.
§ 266.108	Small quantity burner exemption.
§ 266.109	Low risk waste exemption.
§ 266.110	Automatic waiver of DRE trial burn for boilers.
§ 266.111	Standards for direct transfer.

### § 266.112 Regulation of residues.

### § 266.100 - Applicability.

- (a) The regulations of this subpart apply to hazardous waste burned or processed in a boiler or industrial furnace (as defined in §260.10 of this chapter) irrespective of the purpose of burning or processing, except as provided by paragraphs (b), (c), and (d) of this section. In this subpart, the term "burn" means burning for energy recovery or destruction, or processing for materials recovery or as an ingredient. The emissions standards of §§266.104, 266.105, 266.106, and 266.107 apply to facilities operating under interim status or under a RCRA operating permit as specified in §§266.102 and 266.103.
- (b) The following hazardous wastes and facilities are not subject to regulation under this subpart:
- (1) Used oil burned for energy recovery that is also a hazardous waste solely because it exhibits a characteristic of hazardous waste identified in Subpart C of Part 261 of this chapter. Such used oil is subject to regulation under Subpart E of Part 266 rather than this subpart;
- (2) Gas recovered from hazardous or solid waste landfills when such gas is burned for energy recovery.
- (3) Hazardous wastes that are exempt from regulation under §\$261.4 and 261.6(a)(3)(v viii) of this chapter, and hazardous wastes that are subject to the special requirements for conditionally exempt small quantity generators under § 261.5 of this chapter.
- (4) Coke ovens, if the only hazardous waste burned is EPA Hazardous Waste No. K087, decanter tank tar sludge from coking operations.
- (c) Owners and operators of smelting, melting, and refining furnaces (including pyrometallurgical devices such as cupolas, sintering machines, roasters, and foundry furnaces, but not including cement kilns, aggregate kilns, or halogen acid furnaces burning hazardous waste) that process hazardous waste solely for metal recovery are conditionally exempt from regulation under this subpart, except for §§266.101 and 266.112.
  - (1) To be exempt from §§266.102 through 266.111, an owner or operator must:
  - (i) Provide a one-time written notice to the Director indicating the following:
  - (A) The owner or operator claims exemption under this paragraph;
- (B) The hazardous waste is burned solely for metal recovery consistent with the provisions of paragraph (c)(2) of this section;
  - (C) The hazardous waste contains recoverable levels of metals; and
- (D) The owner or operator will comply with the sampling and analysis and recordkeeping requirements of this paragraph;
- (ii) Sample and analyze the hazardous waste and other feedstocks as necessary to comply with the requirements of this paragraph under procedures specified by <u>Test</u>

Methods for Evaluating Solid Waste. Physical/Chemical Methods, SW-846, incorporated by reference in §260.11 of this chapter; and

- (iii) Maintain at the facility for at least three years records to document compliance with the provisions of this paragraph including limits on levels of toxic organic constituents and Btu value of the waste, and levels of recoverable metals in the hazardous waste compared to normal nonhazardous waste feedstocks.
- (2) A hazardous waste meeting either of the following criteria is not processed solely for metal recovery:
- (i) The hazardous waste has a total concentration of organic compounds listed in Part 261, Appendix VIII, of this chapter exceeding 500 ppm by weight, as-generated, and so is considered to be burned for destruction; or
- (ii) The hazardous waste has a heating value of 5,000 Btu/lb or more, as-generated or as-fired into the furnace, and so is considered to be burned as fuel.
- (d) The standards for direct transfer operations under §266.111 apply only to facilities subject to the permit standards of §266.102 or the interim status standards of §266.103.
- (e) The management standards for residues under §266.112 apply to any boiler or industrial furnace burning hazardous waste.

(Approved by the Office of Management and Budget under control number \_\_\_\_\_)

## § 266.101 - Management prior to burning.

- (a) Generators. Generators of hazardous waste that is burned in a boiler or industrial furnace are subject to Part 262 of this chapter.
- (b) Transporters. Transporters of hazardous waste that is burned in a boiler or industrial furnace are subject to Part 263 of this chapter.
- (c) Storage facilities. (1) Owners and operators of facilities that store hazardous waste that is burned in a boiler or industrial furnace are subject to the applicable provisions of Subparts A through L of Part 264, Subparts A through L of Part 265, and Part 270 of this chapter, except as provided by paragraph (c)(2) of this section. These standards apply to storage by the burner as well as to storage facilities operated by intermediaries (processors, blenders, distributors, etc.) between the generator and the burner.
- (2) Owners and operators of facilities that burn, in an on-site boiler or industrial furnace exempt from regulation under the small quantity burner provisions of § 266.108, hazardous waste that they generate are exempt from regulation under Subparts A through L of Part 264, Subparts A through L of Part 265, and Part 270 of this chapter with respect to the storage of mixtures of hazardous waste and the primary fuel to the boiler or industrial furnace in tanks that feed the fuel mixture directly to the burner. Storage of hazardous waste prior to mixing with the primary fuel is subject to regulation as prescribed in paragraph (c)(1) of this section.

#### § 266.102 - Permit standards for burners.

- (a) Applicability. (1) General. Owners and operators of boilers and industrial furnaces burning hazardous waste and not operating under interim status must comply with the requirements of this section and §§ 270.22 and 270.66 of this chapter, unless exempt under the small quantity burner exemption of § 266.108.
- (2) Applicability of Part 264 standards. Owners and operators of boilers and industrial furnaces that burn hazardous waste are subject to the following provisions of Part 264 of this chapter, except as provided otherwise by this subpart:
  - (i) In Subpart A (General), § 264.4;
  - (ii) In Subpart B (General facility standards), §§ 264.11-264.18;
  - (iii) In Subpart C (Preparedness and prevention), §§ 264.31-264.37;
- (iv) In Subpart D (Contingency plan and emergency procedures), §§ 264.51-264.56:
- (v) In Subpart E (Manifest system, recordkeeping, and reporting), the applicable provisions of §§ 264.71-264.77;
  - (vi) In Subpart F (Corrective Action), §§ 264.90 and 264.101;
  - (vii) In Subpart G (Closure and post-closure), §§ 264.111 264.115;
- (viii) In Subpart H (Financial requirements), §§ 264.141, 264.142, 264.143, and 264.147-264.151, except that States and the Federal government are exempt from the requirements of Subpart H; and
- (ix) Subpart BB (Air emission standards for equipment leaks), except §264.1050(a).
- (b) Hazardous waste analysis. (1) The owner or operator must provide an analysis of the hazardous waste that quantifies the concentration of any constituent identified in Appendix VIII of Part 261 of this chapter that may reasonably be expected to be in the waste. Such constituents must be identified and quantified if present, at levels detectable by analytical procedures prescribed by Test Methods for the Evaluation of Solid Waste. Physical/Chemical Methods (incorporated by reference, see §260.11 of this chapter). The Appendix VIII, Part 261 constituents excluded from this analysis must be identified and the basis for their exclusion explained. This analysis will be used to provide all information required by this subpart and § 270.22 and § 270.66 of this chapter and to enable the permit writer to prescribe such permit conditions as necessary to protect human health and the environment. Such analysis must be included as a portion of the Part B permit application, or, for facilities operating under the interim status standards of this subpart, as a portion of the trial burn plan that may be submitted before the Part B application under provisions of §270.66(g) of this chapter as well as any other analysis required by the permit authority in preparing the permit. Owners and operators of boilers and industrial furnaces not operating under the interim status standards must provide the information required by §§270.22 or 270.66(c) of this chapter in the Part B application to the greatest extent possible.

- (2) Throughout normal operation, the owner or operator must conduct sampling and analysis as necessary to ensure that the hazardous waste, other fuels, and industrial furnace feedstocks fired into the boiler or industrial furnace are within the physical and chemical composition limits specified in the permit.
- (c) Emissions standards. Owners and operators must comply with emissions standards provided by §§ 266.104 through 266.107.
- (d) Permits. (1) The owner or operator may burn only hazardous wastes specified in the facility permit and only under the operating conditions specified under paragraph (e) of this section, except in approved trial burns under the conditions specified in § 270.66 of this chapter.
- (2) Hazardous wastes not specified in the permit may not be burned until operating conditions have been specified under a new permit or permit modification, as applicable. Operating requirements for new wastes may be based on either trial burn results or alternative data included with Part B of a permit application under §270.22 of this chapter.
- (3) Boilers and industrial furnaces operating under the interim status standards of §266.103 are permitted under procedures provided by §270.66(g) of this chapter.
- (4) A permit for a new boiler or industrial furnace (those boilers and industrial furnaces not operating under the interim status standards) must establish appropriate conditions for each of the applicable requirements of this section, including but not limited to allowable hazardous waste firing rates and operating conditions necessary to meet the requirements of paragraph (e) of this section, in order to comply with the following standards:
- (i) For the period beginning with initial introduction of hazardous waste and ending with initiation of the trial burn, and only for the minimum time required to bring the device to a point of operational readiness to conduct a trial burn, not to exceed a duration of 720 hours operating time when burning hazardous waste, the operating requirements must be those most likely to ensure compliance with the emission standards of §§ 266.104 through 266.107, based on the Director's engineering judgment. If the applicant is seeking a waiver from a trial burn to demonstrate conformance with a particular emission standard, the operating requirements during this initial period of operation shall include those specified by the applicable provisions of §266.104, §266.105, §266.106, or §266.107. The Director may extend the duration of this period for up to 720 additional hours when good cause for the extension is demonstrated by the applicant.
- (ii) For the duration of the trial burn, the operating requirements must be sufficient to demonstrate compliance with the emissions standards of §§ 266.104 through 266.107 and must be in accordance with the approved trial burn plan;
- (iii) For the period immediately following completion of the trial burn, and only for the minimum period sufficient to allow sample analysis, data computation, submission of the trial burn results by the applicant, review of the trial burn results and modification of the facility permit by the Director to reflect the trial burn results, the operating requirements must be those most likely to ensure compliance with the emission standards of §§ 266.104 through 266.107 based on the Director's engineering judgment.
- (D) For the remaining duration of the permit, the operating requirements must be those demonstrated in a trial burn or by alternative data specified in § 270.22 of this

chapter, as sufficient to ensure compliance with the emissions standards of §§ 266.104 through 266.107.

- (e) Operating requirements. (1) General. A boiler or industrial furnace burning hazardous waste must be operated in accordance with the operating requirements specified in the permit at all times when there is hazardous waste in the unit.
- (2) Requirements to ensure compliance with the organic emissions standards. (i) DRE standard. Operating conditions will be specified either on a case-by-case basis for each hazardous waste burned as those demonstrated (in a trial burn or by alternative data as specified in § 270.22) to be sufficient to comply with the destruction and removal efficiency (DRE) performance standard of § 266.104(a) or as those special operating requirements provided by §266.104(a)(4) for the waiver of the DRE trial burn. When the DRE trial burn is not waived under §266.104(a)(4), each set of operating requirements will specify the composition of the hazardous waste (including acceptable variations in the physical and chemical properties of the hazardous waste which will not affect compliance with the DRE performance standard) to which the operating requirements apply. For each such hazardous waste, the permit will specify acceptable operating limits including, but not limited to, the following conditions as appropriate:
- (A) Feed rate of hazardous waste and other fuels measured and specified as prescribed in paragraph (e)(6) of this section;
- (B) Minimum and maximum device production rate when producing normal product expressed in appropriate units, measured and specified as prescribed in paragraph (e)(6) of this section;
  - (C) Appropriate controls of the hazardous waste firing system;
- (D) Allowable variation in boiler and industrial furnace system design or operating procedures;
- (E) Minimum combustion gas temperature measured at a location indicative of combustion chamber temperature, measured and specified as prescribed in paragraph (e)(6) of this section;
- (F) An appropriate indicator of combustion gas velocity, measured and specified as prescribed in paragraph (e)(6) of this section, unless documentation is provided under \$270.66 of this chapter demonstrating adequate combustion gas residence time; and
- (G) Such other operating requirements as are necessary to ensure that the DRE performance standard of § 266.104(a) is met.
- (ii) Carbon monoxide and hydrocarbon standards. The permit must incorporate a carbon monoxide (CO) limit and, as appropriate, a hydrocarbon (HC) limit as provided by paragraphs (b), (c), (d), (e) and (f) of §266.104. The permit limits will be specified as follows:
- (A) When complying with the CO standard of \$266.104(b)(1), the permit limit is 100 ppmv;
- (B) When complying with the alternative CO standard under \$266.104(c), the permit limit for CO is based on the trial burn and is established as the average over all valid

runs of the highest hourly rolling average CO level of each run, and the permit limit for HC is 20 ppmv (as defined in \$266.104(c)(1)), except as provided in \$266.104(f).

- (C) When complying with the alternative HC limit for industrial furnaces under §266.104(f), the permit limit for HC and CO is the baseline level when hazardous waste is not burned as specified by that paragraph.
- (iii) Start-up and shut-down. During start-up and shut-down of the boiler or industrial furnace, hazardous waste (except waste fed solely as an ingredient under the Tier I (or adjusted Tier I) feed rate screening limits for metals and chloride/chlorine, and except low risk waste exempt from the trial burn requirements under §§266.104(a)(5), 266.105, 266.106, and 266.107) must not be fed into the device unless the device is operating within the conditions of operation specified in the permit.
- (3) Requirements to ensure conformance with the particulate standard. (i) Except as provided in paragraphs (e)(3)(ii) and (iii) of this section, the permit shall specify the following operating requirements to ensure conformance with the particulate standard specified in § 266.105:
- (A) Total ash feed rate to the device from hazardous waste, other fuels, and industrial furnace feedstocks, measured and specified as prescribed in paragraph (e)(6) of this section:
- (B) Maximum device production rate when producing normal product expressed in appropriate units, and measured and specified as prescribed in paragraph (e)(6) of this section:
- (C) Appropriate controls on operation and maintenance of the hazardous waste firing system and any air pollution control system;
- (D) Allowable variation in boiler and industrial furnace system design including any air pollution control system or operating procedures; and
- (E) Such other operating requirements as are necessary to ensure that the particulate standard in § 266.111(b) is met.
- (ii) Permit conditions to ensure conformance with the particulate matter standard shall not be provided for facilities exempt from the particulate matter standard under \$266.105(b);
- (iii) For cement kilns and light-weight aggregate kilns, permit conditions to ensure compliance with the particulate standard shall not limit the ash content of hazardous waste or other feed materials.
- (4) Requirements to ensure conformance with the metals emissions standard. (i) For conformance with the Tier I (or adjusted Tier I) metals feed rate screening limits of paragraphs (b) or (e) of § 266.106, the permit shall specify the following operating requirements:
- (A) Total feed rate of each metal in hazardous waste, other fuels, and industrial furnace feedstocks measured and specified under provisions of paragraph (e)(6) of this section:

- (B) Total feed rate of hazardous waste measured and specified as prescribed in paragraph (e)(6) of this section;
- (C) A sampling and metals analysis program for the hazardous waste, other fuels, and industrial furnace feedstocks:
- (ii) For conformance with the Tier II metals emission rate screening limits under §266.106(c) and the Tier III metals controls under § 266.106(d), the permit shall specify the following operating requirements:
- (A) Maximum emission rate for each metal specified as the average emission rate during the trial burn;
- (B) Feed rate of total hazardous waste and pumpable hazardous waste, each measured and specified as prescribed in paragraph (e)(6)(i) of this section;
- (C) Feed rate of each metal in the following feedstreams, measured and specified as prescribed in paragraphs (e)(6) of this section:
  - (1) Total feed streams:
  - (2) Total hazardous waste feed; and
  - (3) Total pumpable hazardous waste feed;
- (D) Total feed rate of chlorine and chloride in total feed streams measured and specified as prescribed in paragraph (e)(6) of this section;
- (E) Maximum combustion gas temperature measured at a location indicative of combustion chamber temperature, and measured and specified as prescribed in paragraph (e)(6) of this section;
- (F) Maximum flue gas temperature at the inlet to the particulate matter air pollution control system measured and specified as prescribed in paragraph (e)(6) of this section;
- (G) Maximum device production rate when producing normal product expressed in appropriate units and measured and specified as prescribed in paragraph (e)(6) of this section:
- (H) Appropriate controls on operation and maintenance of the hazardous waste firing system and any air pollution control system;
- (I) Allowable variation in boiler and industrial furnace system design including any air pollution control system or operating procedures; and
- (J) Such other operating requirements as are necessary to ensure that the metals standards under §§ 266.106(c) or 266.106(d) are met.
- (iii) For conformance with an alternative implementation approach approved by the Director under \$266.106(f), the permit will specify the following operating requirements:
- (A) Maximum emission rate for each metal specified as the average emission rate during the trial burn;

- (B) Feed rate of total hazardous waste and pumpable hazardous waste, each measured and specified as prescribed in paragraph (e)(6)(i) of this section;
- (C) Feed rate of each metal in the following feedstreams, measured and specified as prescribed in paragraph (e)(6) of this section:
  - (1) Total hazardous waste feed; and
  - (2) Total pumpable hazardous waste feed:
- (D) Total feed rate of chlorine and chloride in total feed streams measured and specified as prescribed in paragraph (e)(6) of this section;
- (E) Maximum combustion gas temperature measured at a location indicative of combustion chamber temperature, and measured and specified as prescribed in paragraph (e)(6) of this section;
- (F) Maximum flue gas temperature at the inlet to the particulate matter air pollution control system measured and specified as prescribed in paragraph (e)(6) of this section;
- (G) Maximum device production rate when producing normal product expressed in appropriate units and measured and specified as prescribed in paragraph (e)(6) of this section:
- (H) Appropriate controls on operation and maintenance of the hazardous waste firing system and any air pollution control system;
- (I) Allowable variation in boiler and industrial furnace system design including any air pollution control system or operating procedures; and
- (J) Such other operating requirements as are necessary to ensure that the metals standards under §§ 266.106(c) or 266.106(d) are met.
- (5) Requirements to ensure conformance with the hydrogen chloride and chlorine gas standards. (i) For conformance with the Tier I total chloride and chlorine feed rate screening limits of § 266.107(b)(1), the permit will specify the following operating requirements:
- (A) Feed rate of total chloride and chlorine in hazardous waste, other fuels, and industrial furnace feedstocks measured and specified as prescribed in paragraph (e)(6) of this section:
- (B) Feed rate of total hazardous waste measured and specified as prescribed in paragraph (e)(6) of this section;
- (C) A sampling and analysis program for total chloride and chlorine for the hazardous waste, other fuels, and industrial furnace feedstocks;
- (ii) For conformance with the Tier II HCl and Cl<sub>2</sub> emission rate screening limits under §266.107(b)(2) and the Tier III HCl and Cl<sub>2</sub> controls under § 266.107(c), the permit will specify the following operating requirements:

- (A) Maximum emission rate for HCl and for Cl<sub>2</sub> specified as the average emission rate during the trial burn;
- (B) Feed rate of total hazardous waste measured and specified as prescribed in paragraph (e)(6) of this section;
- (C) Total feed rate of chlorine and chloride in total feed streams, measured and specified as prescribed in paragraph (e)(6) of this section;
- (D) Maximum device production rate when producing normal product expressed in appropriate units, measured and specified as prescribed in paragraph (e)(6) of this section;
- (E) Appropriate controls on operation and maintenance of the hazardous waste firing system and any air pollution control system;
- (F) Allowable variation in boiler and industrial furnace system design including any air pollution control system or operating procedures; and
- (G) Such other operating requirements as are necessary to ensure that the HCl and Cl<sub>2</sub> standards under §266.107(b)(2) or (c) are met.
- (6) Measuring parameters and establishing limits based on trial burn data. (i) General requirements. As specified in paragraphs (e)(2) through (e)(5) of this section, each operating parameter shall be measured, and permit limits on the parameter shall be established, according to either of the following procedures:
- (A) Instantaneous limits. A parameter may be measured and recorded on an instantaneous basis (i.e., the value that occurs at any time) and the permit limit specified as the time-weighted average during all valid runs of the trial burn; or
- (B) Hourly rolling average. (1) The limit for a parameter may be established and continuously monitored on an hourly rolling average basis defined as follows:
- (i) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.
- (ii) An hourly rolling average is the arithmetic mean of the 60 most recent 1-minute average values recorded by the continuous monitoring system.
- (2) The permit limit for the parameter shall be established based on trial burn data as the average over all valid test runs of the highest hourly rolling average value for each run.
- (ii) Rolling average limits for carcinogenic metals and lead. Feed rate limits for the carcinogenic metals (i.e., arsenic, beryllium, cadmium and chromium) and lead may be established either on an hourly rolling average basis as prescribed by paragraph (e)(6)(i) of this section or on (up to) a 24 hour rolling average basis. If the owner or operator elects to use an averaging period of from 2 to 24 hours:
- (A) The feed rate of each metal shall be limited at any time to ten times the feed rate that would be allowed on a hourly rolling average basis;

- (B) The continuous monitor shall meet the following specifications:
- (1) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.
- (2) The rolling average for the selected averaging period is defined as the arithmetic mean of the most recent one hour block averages for the averaging period. A one hour block average is the arithmetic mean of the one minute averages recorded during the 60-minute period beginning at one minute after the beginning of preceding clock hour, and
- (C) The permit limit for the feed rate of each metal shall be established based on trial burn data as the average over all valid test runs of the highest hourly rolling average feed rate for each run.
- (iii) Feed rate limits for metals, total chloride and chlorine, and ash. Feed rate limits for metals, total chlorine and chloride, and ash are established and monitored by knowing the concentration of the substance (i.e., metals, chloride/chlorine, and ash) in each feedstream and the flow rate of the feedstream. To monitor the feed rate of these substances, the flow rate of each feedstream must be monitored under the continuous monitoring requirements of paragraphs (e)(6)(i) and (ii) of this section.
- (iv) Conduct of trial burn testing. (A) If compliance with all applicable emissions standards of §§266.104 through 266.107 is not demonstrated simultaneously during a set of test runs, the operating conditions of additional test runs required to demonstrate compliance with remaining emissions standards must be as close as possible to the original operating conditions.
- (B) Prior to obtaining test data for purposes of demonstrating compliance with the emissions standards of §§266.104 through 266.107 or establishing limits on operating parameters under this section, the facility must operate under trial burn conditions for a sufficient period to reach steady-state operations. The Director may determine, however, that industrial furnaces that recycle collected particulate matter back into the furnace and that comply with an alternative implementation approach for metals under §266.106(f), need not reach steady state conditions with respect to the flow of metals in the system prior to beginning compliance testing for metals emissions.
- (C) Trial burn data on the level of an operating parameter for which a limit must be established in the permit must be obtained during emissions sampling for the pollutant(s) (i.e., metals, PM, HCl/Cl<sub>2</sub>, organic compounds) for which the parameter must be established as specified by paragraph (e) of this section.
- (7) General requirements. (i) Fugitive emissions. Fugitive emissions must be controlled by:
  - (A) Keeping the combustion zone totally sealed against fugitive emissions; or
  - (B) Maintaining the combustion zone pressure lower than atmospheric pressure; or
- (C) An alternate means of control demonstrated (with Part B of the permit application) to provide fugitive emissions control equivalent to maintenance of combustion zone pressure lower than atmospheric pressure.

- (ii) Automatic waste feed cutoff. A boiler or industrial furnace must be operated with a functioning system that automatically cuts off the hazardous waste feed when operating conditions deviate from those established under this section. The Director may limit the number of cutoffs per an operating period on a case-by-case basis. In addition:
- (A) The permit limit for (the indicator of) minimum combustion chamber temperature must be maintained while hazardous waste or hazardous waste residues remain in the combustion chamber.
- (B) Exhaust gases must be ducted to the air pollution control system operated in accordance with the permit requirements while hazardous waste or hazardous waste residues remain in the combustion chamber; and
- (C) Operating parameters for which permit limits are established must continue to be monitored during the cutoff, and the hazardous waste feed shall not be restarted until the levels of those parameters comply with the permit limits. For parameters that may be monitored on an instantaneous basis, the Director will establish a minimum period of time after a waste feed cutoff during which the parameter must not exceed the permit limit before the hazardous waste feed may be restarted.
- (iii) Changes. A boiler or industrial furnace must cease burning hazardous waste when changes in combustion properties, or feed rates of the hazardous waste, other fuels, or industrial furnace feedstocks, or changes in the boiler or industrial furnace design or operating conditions deviate from the limits as specified in the permit.
- (8) Monitoring and Inspections. (i) The owner or operator must monitor and record the following, at a minimum, while burning hazardous waste:
- (A) If specified by the permit, feed rates and composition of hazardous waste, other fuels, and industrial furnace feedstocks, and feed rates of ash, metals, and total chloride and chlorine:
- (B) If specified by the permit, carbon monoxide (CO), hydrocarbons (HC), and oxygen on a continuous basis at a common point in the boiler or industrial furnace downstream of the combustion zone and prior to release of stack gases to the atmosphere in accordance with operating requirements specified in paragraph (e)(2)(ii) of this section. CO, HC, and oxygen monitors must be installed, operated, and maintained in accordance with methods specified in Methods Manual for Compliance with the BIF Regulations (incorporated by reference, see § 260.11).
- (C) Upon the request of the Director, sampling and analysis of the hazardous waste (and other fuels and industrial furnace feedstocks as appropriate), residues, and exhaust emissions must be conducted to verify that the operating requirements established in the permit achieve the applicable standards of §§ 266.104, 266.105, 266.106, and 266.107.
- (ii) All monitors shall record data in units corresponding to the permit limit unless otherwise specified in the permit.
- (iii) The boiler or industrial furnace and associated equipment (pumps, valves, pipes, fuel storage tanks, etc.) must be subjected to thorough visual inspection when it contains hazardous waste, at least daily for leaks, spills, fugitive emissions, and signs of tampering.

- (iv) The automatic hazardous waste feed cutoff system and associated alarms must be tested at least once every 7 days when hazardous waste is burned to verify operability, unless the applicant demonstrates to the Director that weekly inspections will unduly restrict or upset operations and that less frequent inspections will be adequate. At a minimum, operational testing must be conducted at least once every 30 days.
- (v) These monitoring and inspection data must be recorded and the records must be placed in the operating record required by §264.73 of this chapter.
- (9) Direct transfer to the burner. If hazardous waste is directly transferred from a transport vehicle to a boiler or industrial furnace without the use of a storage unit, the owner and operator must comply with §266.111.
- (10) Recordkeeping. The owner or operator must keep in the operating record of the facility all information and data required by this section for not less than three years.
- (11) Closure. At closure, the owner or operator must remove all hazardous waste and hazardous waste residues (including, but not limited to, ash, scrubber waters, and scrubber sludges) from the boiler or industrial furnace.

(Approved by the Office of Management and Budget under control number \_\_\_\_\_\_

- § 266.103 Interim status standards for owners and operators of facilities that burn hazardous waste in a boiler or industrial furnace.
- (a) Purpose, scope, applicability. (1) General. (i) The purpose of this section is to establish minimum national standards for owners and operators of "existing" boilers and industrial furnaces that burn hazardous waste where such standards define the acceptable management of hazardous waste during the period of interim status. The standards of this section apply to owners and operators of existing facilities until either a permit is issued under § 266.102(d) or until closure responsibilities identified in this section are fulfilled.
- (ii) Existing or in existence means a boiler or industrial furnace that on or before [insert date 6 months after promulgation of this rule] is either in operation burning or processing hazardous waste or for which construction (including the ancillary facilities to burn or process the hazardous waste) has commenced. A facility has commenced construction if the owner or operator has obtained the Federal, State, and local approvals or permits necessary to begin physical construction; and either:
  - (A) A continuous on-site, physical construction program has begun; or
- (B) The owner or operator has entered into contractual obligations—which cannot be canceled or modified without substantial loss—for physical construction of the facility to be completed within a reasonable time.
- (iii) If a boiler or industrial furnace is located at a facility that already has a permit or interim status, then the facility must comply with the applicable regulations dealing with permit modifications in § 270.42 or changes in interim status in § 270.72 of this chapter.
- (2) Exemptions. The requirements of this section do not apply to hazardous waste and facilities exempt under §§ 266.100(b), (c) or 266.108.

- (3) Prohibition on burning dioxin-listed wastes. Hazardous waste listed for dioxin or derived from any of the following dioxin-listed wastes may not be burned in a boiler or industrial furnace operating under interim status: EPA Hazardous Waste Numbers F020, F021, F022, F023, F026, or F027.
- (4) Applicability of Part 265 standards. Owners and operators of boilers and industrial furnaces that burn hazardous waste and are operating under interim status are subject to the following provisions of Part 265 of this chapter, except as provided otherwise by this section:
  - (i) In Subpart A (General), §265.4;
  - (ii) In Subpart B (General facility standards), §§265.11-265.17;
  - (iii) In Subpart C (Preparedness and prevention), §§265.31-265.37;
- (iv) In Subpart D (Contingency plan and emergency procedures), §\$265.51-265.56:
- (v) In Subpart E (Manifest system, recordkeeping, and reporting), §\$265.71-265.77, except that §\$265.71, 265.72, and 265.76 do not apply to owners and operators of on-site facilities that do not receive any hazardous waste from off-site sources;
  - (vi) In Subpart G (Closure and post-closure), §§ 265.111-265.115;
- (vii) In Subpart H (Financial requirements), §§ 265.141, 265.142, 265.143, and 265.147-265.151, except that States and the Federal government are exempt from the requirements of Subpart H; and
- (viii) Subpart BB (Air emission standards for equipment leaks), except §265.1050(a).
- (5) Special requirements for furnaces. The following controls apply during interim status to industrial furnaces (e.g., kilns, cupolas) that feed hazardous waste for a purpose other than solely as an ingredient (see paragraph (a)(5)(ii) of this section) at any location other than the hot end where products are normally discharged and where fuels are normally fired:
- (i) Controls. (A) The hazardous waste shall be fed at a location where combustion gas temperatures are at least 1800°F;
- (B) The owner or operator must determine that adequate oxygen is present in combustion gases to combust organic constituents in the waste and retain documentation of such determination in the facility record;
  - (C) For cement kiln systems, the hazardous waste shall be fed into the kiln; and
- (D) The hydrocarbon controls of \$266.104(c) or paragraph (c)(7)(ii) of this section apply upon certification of compliance under paragraph (c) of this section irrespective of the CO level achieved during the compliance test.
- (ii) Burning hazardous waste solely as an ingredient. A hazardous waste is burned for a purpose other than solely as an ingredient if it meets either of these criteria:

- (A) The hazardous waste has a total concentration of nonmetal compounds listed in Part 261, Appendix VIII, of this chapter exceeding 500 ppm by weight as-generated (and, so, is considered to be burned for destruction); or
- (B) The hazardous waste has a heating value of 5,000 Btu/lb or more, as-generated or as-fired (and, so, is considered to be burned as fuel).
- (6) Restrictions on burning hazardous waste that is not a fuel. Prior to certification of compliance under paragraph (c) of this section, owners and operators shall not feed hazardous waste (other than hazardous waste burned solely as an ingredient) in a boiler or industrial furnace that has a heating value less than 5,000 Btu/lb, as-generated, except for purposes of compliance testing (or testing prior to compliance testing) for a total period of time not to exceed 720 hours.
- (7) Direct transfer to the burner. If hazardous waste is directly transferred from a transport vehicle to a boiler or industrial furnace without the use of a storage unit, the owner and operator must comply with §266.111.
- (b) Certification of precompliance. (1) General. The owner or operator must provide complete and accurate information specified in paragraph (b)(2) of this section to the Director on or before [the effective date of this rule], and must establish limits for the operating parameters specified in paragraph (b)(3) of this section. Such information is termed a "certification of precompliance" and constitutes a certification that the owner or operator has determined that, when the facility is operated within the limits specified in paragraph (b)(3) of this section, the owner or operator believes that, using best engineering judgment, emissions of particulate matter, metals, and HCl and Cl2 are not likely to exceed the limits provided by §§266.105, 266.106, and 266.107. The facility may burn hazardous waste only under the operating conditions that the owner or operator establishes under paragraph (b)(3) of this section until the owner or operator submits a revised certification of precompliance under paragraph (b)(8) of this section or a certification of compliance under paragraph (c) of this section, or until a permit is issued.
- (2) Information required. The following information must be submitted with the certification of precompliance to support the determination that the limits established for the operating parameters identified in paragraph (b)(3) are not likely to result in an exceedance of the allowable emission rates for particulate matter, metals, and HCl and Cl<sub>2</sub>:
  - (i) General facility information:
  - (A) EPA facility ID number.
  - (B) Facility name, contact person, telephone number, and address;
- (C) Description of boilers and industrial furnaces burning hazardous waste, including type and capacity of device;
- (D) A scaled plot plan showing the entire facility and location of the boilers and industrial furnaces burning hazardous waste; and
- (E) A description of the air pollution control system on each device burning hazardous waste, including the temperature of the flue gas at the inlet to the particulate matter control system.

- (ii) Except for facilities complying with the Tier I feed rate screening limits for metals or total chlorine and chloride provided by §§266.106(b) or (e) and 266.107(b)(1) or (e) respectively, the estimated uncontrolled (at the inlet to the air pollution control system) emissions of particulate matter, each metal controlled by §266.106, and hydrogen chloride and chlorine, and the following information to support such determinations:
- (A) The feed rate (lb/hr) of ash, chlorine, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, thallium in each feedstream (hazardous waste, other fuels, industrial furnace feedstocks);
- (B) The estimated partitioning factor to the combustion gas for the materials identified in paragraph (b)(ii)(A) of this section and the basis for the estimate and an estimate of the partitioning to HCl and Cl<sub>2</sub> of total chloride and chlorine in feed materials. To estimate the partitioning factor, the owner or operator must use either best engineering judgment or the procedures specified in Methods Manual for Compliance with the BIF Regulations (incorporated by reference, see §260.11).
- (C) For industrial furnaces that recycle collected particulate matter (PM) back into the furnace, the estimated enrichment factor for each metal. To estimate the enrichment factor, the owner or operator must use either best engineering judgment or the procedures specified in "Alternative Methodology for Implementing Metals Controls" in Methods Manual for Compliance with the BIF Regulations (incorporated by reference in §266.11).
- (D) If best engineering judgment is used to estimate partitioning factors or enrichment factors under paragraphs (b)(ii)(B) or (b)(ii)(C) respectively, the basis for the judgment. When best engineering judgment is used to develop or evaluate data or information and make determinations under this section, the determinations must be made by a qualified, registered professional engineer and a certification of his/her determinations in accordance with §270.11(d) of this chapter must be provided in the certification of precompliance.
- (iii) For facilities complying with the Tier I feed rate screening limits for metals or total chlorine and chloride provided by §\$266.106(b) or (e) and 266.107(b)(1) or (e), the feed rate (lb/hr) of total chloride and chlorine, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium in each feedstream (hazardous waste, other fuels, industrial furnace feedstocks).
- (iv) For facilities complying with the Tier II or Tier III emission limits for metals or HCl and Cl<sub>2</sub> (under §\$266.106(c) or (d) or 266.107(b)(2) or (c)), the estimated controlled (outlet of the air pollution control system) emissions rates of particulate matter, each metal controlled by \$266.106, and HCl and Cl<sub>2</sub>, and the following information to support such determinations:
- (A) The estimated air pollution control system (APCS) removal efficiency for particulate matter, HCl, Cl<sub>2</sub>, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium.
- (B) To estimate APCS removal efficiency, the owner or operator must use either best engineering judgment or the procedures prescribed in <u>Methods Manual for Compliance</u> with the BIF Regulations (incorporated by reference, see §260.11).

- (C) If best engineering judgment is used to estimate APCS removal efficiency, the basis for the judgment. Use of best engineering judgment must be in conformance with provisions of paragraph (b)(2)(ii)(D) of this section.
- (v) Determination of allowable emissions rates for HCl, Cl<sub>2</sub>, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium, and the following information to support such determinations:
  - (A) For all facilities:
  - (1) Physical stack height;
  - (2) Good engineering practice stack height as defined by 40 CFR 51.100(ii);
  - (3) Maximum flue gas flow rate;
  - (4) Maximum flue gas temperature;
- (5) Attach a US Geological Service topographic map (or equivalent) showing the facility location and surrounding land within 5 km of the facility.
  - (6) Identify terrain type: complex or noncomplex; and
  - (7) Identify land use: urban or rural.;
- (B) For owners and operators using Tier III site specific dispersion modeling to determine allowable levels under §266.106(d) or §266.107(c), or adjusted Tier I feed rate screening limits under §§266.106(e) or 266.107(e):
  - (1) Dispersion model and version used;
  - (2) Source of meteorological data;
- (3) The dilution factor in micrograms per cubic meter per gram per second of emissions for the maximum annual average off-site (unless on-site is required) ground level concentration (MEI location); and
  - (4) Indicate the MEI location on the map required under paragraph (b)(2)(v)(A)(5);
- (vi) For facilities complying with the Tier II or III emissions rate controls for metals or HCl and Cl<sub>2</sub>, a comparison of the estimated controlled emissions rates determined under paragraph (b)(2)(iv) with the allowable emission rates determined under paragraph (b)(2)(v);
- (vii) For facilities complying with the Tier I (or adjusted Tier I) feed rate screening limits for metals or total chloride and chlorine, a comparison of actual feed rates of each metal and total chlorine and chloride determined under paragraph (b)(2)(iii) to the Tier I allowable feed rates; and
- (viii) For industrial furnaces that feed hazardous waste for any purpose other than solely as an ingredient (as defined by paragraph (a)(5)(ii) of this section) at any location

other than the product discharge end of the device, documentation of compliance with the requirements of paragraphs (a)(5)(i)(A), (B), and (C) of this section.

- (ix) For industrial furnaces that recycle collected particulate matter (PM) back into the furnace and that will certify compliance with the metals emissions standards under paragraph (c)(3)(ii)(A) of this section:
  - (A) The applicable particulate matter standard in lb/hr, and
  - (B) The precompliance limit on the concentration of each metal in collected PM.
- (3) Limits on operating conditions. The owner and operator shall establish limits on the following parameters consistent with the determinations made under paragraph (b)(2) of this section and certify (under provisions of paragraph (b)(9) of this section) to the Director that the facility will operate within the limits during interim status when there is hazardous waste in the unit until revised certification of precompliance under paragraph (b)(8) of this section or certification of compliance under paragraph (c) of this section:
- (i) Feed rate of total hazardous waste and (unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under §266.106(b) or (e)) pumpable hazardous waste:
  - (ii) Feed rate of each metal in the following feed streams:
- (A) Total feed streams, except that industrial furnaces that must comply with the alternative metals implementation approach under paragraph (b)(4) of this section must specify limits on the concentration of each metal in collected particulate matter in lieu of feed rate limits for total feedstreams:
  - (B) Total hazardous waste feed; and
- (C) Total pumpable hazardous waste feed, unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under §266.106(b) or (e);
  - (iii) Total feed rate of chlorine and chloride in total feed streams;
- (iv) Total feed rate of ash in total feed streams, except that the ash feed rate for cement kilns and light-weight aggregate kilns is not limited; and
- (v) Maximum production rate of the device in appropriate units when producing normal product.
- (4) Operating requirements for furnaces that recycle PM. Owners and operators of furnaces that recycle collected particulate matter (PM) back into the furnace and that will certify compliance with the metals emissions controls under paragraph (c)(3)(ii)(A) of this section must comply with the special operating requirements provided in "Alternative Methodology for Implementing Metals Controls" in Methods Manual for Compliance with the BIF Regulations (incorporated by reference in §260.11).
- (5) Measurement of feed rates and production rate. (i) General requirements. Limits on each of the parameters specified in paragraph (b)(3) of this section (except for limits on metals concentrations in collected particulate matter (PM) for industrial furnaces that recycle collected PM) shall be established and continuously monitored under either of the following methods:

- (A) Instantaneous limits. A limit for a parameter may be established and continuously monitored on an instantaneous basis (i.e., the value that occurs at any time) not to be exceeded at any time; or
- (B) Hourly rolling average limits. A limit for a parameter may be established and continuously monitored on an hourly rolling average basis defined as follows:
- (I) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.
- (2) An hourly rolling average is the arithmetic mean of the 60 most recent 1-minute average values recorded by the continuous monitoring system.
- (ii) Rolling average limits for carcinogenic metals and lead. Feed rate limits for the carcinogenic metals (arsenic, beryllium, cadmium, and chromium) and lead may be established either on an hourly rolling average basis as prescribed by paragraph (e)(5)(i)(B) or on (up to) a 24 hour rolling average basis. If the owner or operator elects to use an averaging period from 2 to 24 hours:
- (A) The feed rate of each metal shall be limited at any time to ten times the feed rate that would be allowed on a hourly rolling average basis;
  - (B) The continuous monitor shall meet the following specifications:
- (1) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.
- (2) The rolling average for the selected averaging period is defined as the arithmetic mean of the most recent one hour block averages for the averaging period. A one hour block average is the arithmetic mean of the one minute averages recorded during the 60-minute period beginning at one minute after the beginning of preceding clock hour.
- (iii) Feed rate limits for metals, total chloride and chlorine, and ash. Feed rate limits for metals, total chlorine and chloride, and ash are established and monitored by knowing the concentration of the substance (i.e., metals, chloride/chlorine, and ash) in each feedstream and the flow rate of the feedstream. To monitor the feed rate of these substances, the flow rate of each feedstream must be monitored under the continuous monitoring requirements of paragraphs (b)(5)(i) and (ii) of this section.
- (6) Public notice requirements at precompliance. On or before [the effective date of this rule] the owner or operator must submit a notice with the following information for publication in a major local newspaper of general circulation and send a copy of the notice to the appropriate units of State and local government. The owner and operator must provide to the Director with the certification of precompliance evidence of submitting the notice for publication. The notice, which shall be entitled "Notice of Certification of Precompliance with Hazardous Waste Burning Requirements of 40 CFR 266.103(b)", must include:
- (i) Name and address of the owner and operator of the facility as well as the location of the device burning hazardous waste;

- (ii) Date that the certification of precompliance is submitted to the Director,
- (iii) Brief description of the regulatory process required to comply with the interim status requirements of this section including required emissions testing to demonstrate conformance with emissions standards for organic compounds, particulate matter, metals, and HCl and Cl<sub>2</sub>;
- (iv) Types and quantities of hazardous waste burned including, but not limited to, source, whether solids or liquids, as well as an appropriate description of the waste;
- (v) Type of device(s) in which the hazardous waste is burned including a physical description and maximum production rate of each device;
- (vi) Types and quantities of other fuels and industrial furnace feedstocks fed to each unit:
- (vii) Brief description of the basis for this certification of precompliance as specified in paragraph (b)(2) of this section;
- (viii) Locations where the operating record for the facility can be viewed and copied by interested parties. These locations shall at a minimum include:
- (A) The Agency office where the supporting documentation was submitted or another location designated by the Director; and
  - (B) The facility site where the device is located;
- (ix) Notification of the establishment of a facility mailing list whereby interested parties shall notify the Agency that they wish to be placed on the mailing list to receive future information and notices about this facility; and
- (x) Location (mailing address) of the applicable EPA Regional Office, Hazardous Waste Division, where further information can be obtained on EPA regulation of hazardous waste burning.
- (7) Monitoring other operating parameters. When the monitoring systems for the operating parameters listed in paragraphs (c)(1)(v through xiii) of this section are installed and operating in conformance with vendor specifications or (for CO, HC, and oxygen) specifications provided by the Methods Manual for Compliance with the BIF Regulations (incorporated by reference, see §260.11), as appropriate, the parameters shall be continuously monitored and records shall be maintained in the operating record.
- (8) Revised certification of precompliance. The owner or operator may revise at any time the information and operating conditions documented under paragraphs (b)(2) and (b)(3) of this section in the certification of precompliance by submitting a revised certification of precompliance under procedures provided by those paragraphs.
- (i) The public notice requirements of paragraph (b)(6) of this section do not apply to recertifications.
- (ii) The owner and operator must operate the facility within the limits established for the operating parameters under paragraph (b)(3) of this section until a revised certification

is submitted under this paragraph or a certification of compliance is submitted under paragraph (c) of this section.

- (9) Certification of precompliance statement. The owner or operator must include the following signed statement with the certification of precompliance submitted to the Director:
- " I certify under penalty of law that this information was prepared under my direction or supervision in accordance with a system designed to ensure that qualified personnel properly gathered and evaluated the information and supporting documentation. Copies of all emissions tests, dispersion modeling results and other information used to determine conformance with the requirements of §266.103(b) are available at the facility and can be obtained from the facility contact person listed above. Based on my inquiry of the person or persons who manages the facility, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

I also acknowledge that the operating limits established in this certification pursuant to §266.103(b)(3) and (4) are enforceable limits at which the facility can legally operate during interim status until: (1) a revised certification of precompliance is submitted, (2) a certification of compliance is submitted, or (3) an operating permit is issued."

- (c) Certification of compliance. On or before [date 18 months after promulgation of the rule], the owner or operator shall conduct emissions testing to document compliance with the emissions standards of §§266.104(b) through (e), 266.105, 266.106, 266.107, and paragraph (a)(5)(i)(D) of this section, under the procedures prescribed by this paragraph, except under extensions of time provided by paragraph (c)(7). Based on the compliance test, the owner or operator shall submit to the Director a complete and accurate "certification of compliance" (under paragraph (c)(4) of this section) with those emission standards establishing limits on the operating parameters specified in paragraph (c)(1).
- (1) Limits on operating conditions. The owner or operator shall establish limits on the following parameters based on operations during the compliance test (under procedures prescribed in paragraph (c)(4)(iv) of this section) and include these limits with the certification of compliance. The boiler or industrial furnace must be operated in accordance with these operating limits at all times when there is hazardous waste in the unit until an operating permit is issued.
- (i) Feed rate of total hazardous waste and (unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under \$266.106(b) or (e)), pumpable hazardous waste;
  - (ii) Feed rate of each metal in the following feedstreams:
- (A) Total feedstreams, except that industrial furnaces that must comply with the alternative metals implementation approach under paragraph (c)(3)(ii) of this section must specify limits on the concentration of each metal in collected particulate matter in lieu of feed rate limits for total feedstreams;
- (B) Total hazardous waste feed (unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under §266.106(b) or (e)); and

- (C) Total pumpable hazardous waste feed;
- (iii) Total feed rate of chlorine and chloride in total feed streams;
- (iv) Total feed rate of ash in total feed streams, except that the ash feed rate for cement kilns and light-weight aggregate kilns is not limited;
- (v) Carbon monoxide concentration, and where required, hydrocarbon concentration in stack gas. When complying with the CO controls of §266.104(b), the CO limit is 100 ppmv, and when complying with the HC controls of §266.104(c), the HC limit is 20 ppmv. When complying with the CO controls of §266.104(c), the CO limit is established based on the compliance test;
- (vi) Maximum production rate of the device in appropriate units when producing normal product;
- (vii) Maximum combustion chamber temperature where the temperature measurement is as close to the combustion zone as possible and is upstream of any quench water injection, except for boilers and industrial furnaces that have only pumpable liquid or gaseous feed streams (unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under §266.106(b) or (e));
- (viii) Maximum flue gas temperature entering a particulate matter control device (unless complying with Tier I or adjusted Tier I metals feed rate screening limits under §266.106(b) or (e));
- (ix) For systems using wet scrubbers, including wet ionizing scrubbers (unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under \$266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under \$266.107(b)(1) or (e)):
  - (A) Minimum liquid to flue gas ratio;
- (B) Minimum scrubber blowdown from the system or maximum suspended solids content of the scrubber water; and
  - (C) Minimum pH level of the scrubber water,
- (x) For systems using venturi scrubbers, the minimum differential gas pressure across the venturi (unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under \$266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under \$266.107(b)(1) or (e));
- (xi) For systems using dry scrubbers (unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under \$266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under \$266.107(b)(1) or (e)):
  - (A) Minimum caustic feed rate; and
  - (B) Maximum flue gas flow rate;
- (xii) For systems using wet ionizing scrubbers or electrostatic precipitators (unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under

- \$266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under \$266.107(b)(1) or (e)):
- (A) Minimum electrical power in kilovolt amperes (kVA) to the precipitator plates; and
  - (B) Maximum flue gas flow rate;
- (xiii) For systems using fabric filters (baghouses), the minimum pressure drop (unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under \$266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under \$266.107(b)(1) or (e)).
- (2) Prior notice of compliance testing. At least 30 days prior to the compliance testing required by paragraph (c)(3) of this section, the owner or operator shall notify the Director and submit the following information:
  - (i) General facility information including:
  - (A) EPA facility ID number:
  - (B) Facility name, contact person, telephone number, and address;
- (C) Person responsible for conducting compliance test, including company name, address, and telephone number, and a statement of qualifications;
  - (D) Planned date of the compliance test;
  - (ii) Specific information on each device to be tested including:
  - (A) Description of boiler or industrial furnace;
- (B) A scaled plot plan showing the entire facility and location of the boiler or industrial furnace;
  - (C) A description of the air pollution control system:
  - (D) Identification of the continuous emission monitors that are installed, including:
  - (1) Carbon monoxide monitor.
  - (2) Oxygen monitor,
- (3) Hydrocarbon monitor, specifying the minimum temperature of the system and, if the temperature is less than 150°C, an explanation of why a heated system is not used (see paragraph (c)(5) of this section) and a brief description of the sample gas conditioning system;
- (E) Indication of whether the stack is shared with another device that will be in operation during the compliance test;
  - (F) Other information useful to an understanding of the system design or operation.

- (iii) Information on the testing planned, including a complete copy of the test protocol and Quality Assurance/Quality Control (QA/QC) plan, and a summary description for each test providing the following information at a minimum:
- (A) Purpose of the test (e.g., demonstrate compliance with emissions of particulate matter); and
- (B) Planned operating conditions, including levels for each pertinent parameter specified in paragraph (c)(1) of this section.
- (3) Compliance testing. (i) General. Compliance testing must be conducted under conditions for which the owner or operator has submitted a certification of precompliance under paragraph (b) of this section and under conditions established in the notification of compliance testing required by paragraph (c)(2) of this section.
- (ii) Special requirements for industrial furnaces that recycle collected PM. Owners and operators of industrial furnaces that recycle back into the furnace particulate matter (PM) from the air pollution control system must comply with one of the following procedures for testing to determine compliance with the metals standards of §266.106(c) or (d):
- (A) The special testing requirements prescribed in "Alternative Method for Implementing Metals Controls" in Methods Manual for Compliance with the BIF Regulations (incorporated by reference in §260.11); or
- (B) Stack emissions testing for a minimum of 6 hours each day while hazardous waste is burned during interim status. The testing must be conducted when burning normal hazardous waste for that day at normal feed rates for that day and when the air pollution control system is operated under normal conditions. During interim status, hazardous waste analysis for metals content must be sufficient for the owner or operator to determine if changes in metals content may affect the ability of the facility to meet the metals emissions standards established under \$266.106(c) or (d). Under this option, operating limits (under paragraph (c)(1)) must be established during compliance testing under paragraph (c)(3) only on the following parameters:
  - (1) Feed rate of total hazardous waste;
  - (2) Total feed rate of chlorine and chloride in total feed streams;
- (3) Total feed rate of ash in total feed streams, except that the ash feed rate for cement kilns and light-weight aggregate kilns is not limited;
- (4) Carbon monoxide concentration, and where required, hydrocarbon concentration in stack gas;
- (5) Maximum production rate of the device in appropriate units when producing normal product; or
- (C) Conduct compliance testing to determine compliance with the metals standards to establish limits on the operating parameters of paragraph (c)(1) only after the kiln system has been conditioned to enable it to reach equilibrium with respect to metals fed into the system and metals emissions. During conditioning, hazardous waste and raw materials

having the same metals content as will be fed during the compliance test must be fed at the feed rates that will be fed during the compliance test.

- (iii) Conduct of compliance testing. (A) If compliance with all applicable emissions standards of §§266.104 through 266.107 is not demonstrated simultaneously during a set of test runs, the operating conditions of additional test runs required to demonstrate compliance with remaining emissions standards must be as close as possible to the original operating conditions.
- (B) Prior to obtaining test data for purposes of demonstrating compliance with the applicable emissions standards of §§266.104 through 266.107 or establishing limits on operating parameters under this section, the facility must operate under compliance test conditions for a sufficient period to reach steady-state operations. Industrial furnaces that recycle collected particulate matter back into the furnace and that comply with paragraphs (c)(3)(ii)(A) or (B) or this section, however, need not reach steady state conditions with respect to the flow of metals in the system prior to beginning compliance testing for metals.
- (C) Compliance test data on the level of an operating parameter for which a limit must be established in the certification of compliance must be obtained during emissions sampling for the pollutant(s) (i.e., metals, PM, HCl/Cl<sub>2</sub>, organic compounds) for which the parameter must be established as specified by paragraph (c)(1) of this section.
- (4) Certification of compliance. Within 90 days of completing compliance testing, the owner or operator must certify to the Director compliance with the emissions standards of §§266.104(b), (c), and (e), 266.105, 266.106, 266.107, and paragraph (a)(5)(i)(D) of this section. The certification of compliance must include the following information:
  - (i) General facility and testing information including:
  - (A) EPA facility ID number;
  - (B) Facility name, contact person, telephone number, and address;
- (C) Person responsible for conducting compliance test, including company name, address, and telephone number, and a statement of qualifications;
  - (D) Date(s) of each compliance test;
  - (E) Description of boiler or industrial furnace tested;
- (F) Person responsible for quality assurance/quality control (QA/QC), title, and telephone number, and statement that procedures prescribed in the QA/QC plan submitted under \$266.103(c)(2)(iii) have been followed, or a description of any changes and an explanation of why changes were necessary.
- (G) Description of any changes in the unit configuration prior to or during testing that would alter any of the information submitted in the prior notice of compliance testing under paragraph (c)(2) of this section, and an explanation of why the changes were necessary;
- (H) Description of any changes in the planned test conditions prior to or during the testing that alter any of the information submitted in the prior notice of compliance testing

under paragraph (c)(2) of this section, and an explanation of why the changes were necessary; and

- (I) The complete report on results of emissions testing.
- (ii) Specific information on each test including:
- (A) Purpose(s) of test (e.g., demonstrate conformance with the emissions limits for particulate matter, metals, HCl, Cl<sub>2</sub>, and CO)
- (B) Summary of test results for each run and for each test including the following information:
  - (1) Date of run:
  - (2) Duration of run:
- (3) Time-weighted average and highest hourly rolling average CO level for each run and for the test:
- (4) Highest hourly rolling average HC level, if HC monitoring is required for each run and for the test:
- (5) If dioxin and furan testing is required under §266.104(e), time-weighted average emissions for each run and for the test of chlorinated dioxin and furan emissions, and the predicted maximum annual average ground level concentration of the toxicity equivalency factor;
  - (6) Time-weighted average particulate matter emissions for each run and for the test;
  - (7) Time-weighted average HCl and Cl2 emissions for each run and for the test;
- (8) Time-weighted average emissions of the metals subject to regulation under §266.107 for each run and for the test; and
  - (9) QA/QC results.
- (iii) Comparison of the actual emissions during each test with the emissions limits prescribed by §§266.104(b), (c), and (e), 266.105, 266.106, and 266.107 and established for the facility in the certification of precompliance under paragraph (b) of this section.
- (iv) Determination of operating limits based on all valid runs of the compliance test for each applicable parameter listed in paragraph (c)(1) of this section using either of the following procedures:
- (A) Instantaneous limits. A parameter may be measured and recorded on an instantaneous basis (i.e., the value that occurs at any time) and the operating limit specified as the time-weighted average during all runs of the compliance test; or
- (B) Hourly rolling average basis. (1) The limit for a parameter may be established and continuously monitored on an hourly rolling average basis defined as follows:

- (i) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.
- (ii) An hourly rolling average is the arithmetic mean of the 60 most recent 1-minute average values recorded by the continuous monitoring system.
- (2) The operating limit for the parameter shall be established based on compliance test data as the average over all test runs of the highest hourly rolling average value for each run.
- (C) Rolling average limits for carcinogenic metals and lead. Feed rate limits for the carcinogenic metals (i.e., arsenic, beryllium, cadmium and chromium) and lead may be established either on an hourly rolling average basis as prescribed by paragraph (c)(4)(iv)(B) of this section or on (up to) a 24 hour rolling average basis. If the owner or operator elects to use an averaging period of from 2 to 24 hours:
- (1) The feed rate of each metal shall be limited at any time to ten times the feed rate that would be allowed on a hourly rolling average basis;
  - (2) The continuous monitor shall meet the following specifications:
- (i) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.
- (ii) The rolling average for the selected averaging period is defined as the arithmetic mean of the most recent one hour block averages for the averaging period. A one hour block average is the arithmetic mean of the one minute averages recorded during the 60-minute period beginning at one minute after the beginning of preceding clock hour, and
- (3) The operating limit for the feed rate of each metal shall be established based on compliance test data as the average over all test runs of the highest hourly rolling average feed rate for each run.
- (D) Feed rate limits for metals, total chloride and chlorine, and ash. Feed rate limits for metals, total chlorine and chloride, and ash are established and monitored by knowing the concentration of the substance (i.e., metals, chloride/chlorine, and ash) in each feedstream and the flow rate of the feedstream. To monitor the feed rate of these substances, the flow rate of each feedstream must be monitored under the continuous monitoring requirements of paragraphs (c)(4)(iv)(A) through (C) of this section.
- (v) Certification of compliance statement. The following statement shall accompany the certification of compliance:

"I certify under penalty of law that this information was prepared under my direction or supervision in accordance with a system designed to ensure that qualified personnel properly gathered and evaluated the information and supporting documentation. Copies of all emissions tests, dispersion modeling results and other information used to determine conformance with the requirements of \$266.103(c) are available at the facility and can be obtained from the facility contact person listed above. Based on my inquiry of the person or persons who manages the facility, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and

belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

I also acknowledge that the operating conditions established in this certification pursuant to §266.103(c)(4)(iv) are enforceable limits at which the facility can legally operate during interim status until a revised certification of compliance is submitted."

- (5) Special requirements for HC monitoring systems. When an owner or operator is required to comply with the hydrocarbon (HC) controls provided by §\$266.104(c) or paragraph (a)(5)(i)(D) of this section, a conditioned gas monitoring system may be used in conformance with specifications provided in Methods Manual for Compliance with the BIF Regulations (incorporated by reference, see §260.11) provided that the owner or operator submits a certification of compliance without using extensions of time provided by paragraph (c)(7) of this section.
- (6) Special operating requirements for industrial furnaces that recycle collected PM. Owners and operators of industrial furnaces that recycle back into the furnace particulate matter (PM) from the air pollution control system must:
- (i) When complying with the requirements of paragraph (c)(3)(ii)(A) of this section, the operating requirements prescribed in "Alternative Method to Implement the Metals Controls" in Methods Manual for Compliance with the BIF Regulations (incorporated by reference in §260.11); and
- (ii) When complying with the requirements of paragraph (c)(3)(ii)(B) of this section, the operating requirements prescribed by that paragraph.
- (7) Extensions of time. (i) If the owner or operator does not submit a complete certification of compliance for all of the applicable emissions standards of §\$266.104, 266.105, 266.106, and 266.107 by [insert date 18 months from promulgation], he/she must either:
- (A) Stop burning hazardous waste and begin closure activities under paragraph (l) of this section for the hazardous waste portion of the facility; or
- (B) Limit hazardous waste burning to a total period of 720 hours for the period of time beginning [insert date 18 months from promulgation], submit a notification to the Director by [insert date 18 months from promulgation] stating that the facility is operating under restricted interim status and intends to resume burning hazardous waste, and submit a complete certification of compliance by [insert date 30 months from promulgation]; or
- (C) Obtain a case-by-case extension of time under paragraph (c)(7)(ii) of this section.
- (ii) The owner or operator may request a case-by-case extension of time to extend any time limit provided by paragraph (c) of this section if compliance with the time limit is not practicable for reasons beyond the control of the owner or operator.
- (A) In granting an extension, the Director may apply conditions as the facts warrant to ensure timely compliance with the requirements of this section and that the facility operates in a manner that does not pose a hazard to human health and the environment;

- (B) When an owner and operator request an extension of time to enable them to obtain a RCRA operating permit because the facility cannot meet the HC limit of §266.104(f) of this chapter:
  - (1) The Director shall, in considering whether to grant the extension:
- (i) Determine whether the owner and operator have submitted in a timely manner a complete Part B permit application that includes information required under §270.22(b) of this chapter; and
- (ii) Consider whether the owner and operator have made a good faith effort to certify compliance with all other emission controls, including the controls on dioxins and furans of §266.104(e) and the controls on PM, metals, and HCl/Cl<sub>2</sub>.
- (2) If an extension is granted, the Director shall, as a condition of the extension, require the facility to operate under flue gas concentration limits on CO and HC that, based on available information, including information in the Part B permit application, are baseline CO and HC levels as defined by §266.104(f)(1).
- (8) Revised certification of compliance. The owner or operator may submit at any time a revised certification of compliance (recertification of compliance) under the following procedures:
- (i) Prior to submittal of a revised certification of compliance, hazardous waste may not be burned for more than a total of 720 hours under operating conditions that exceed those established under a current certification of compliance, and such burning may be conducted only for purposes of determining whether the facility can operate under revised conditions and continue to meet the applicable emissions standards of §§266.104, 266.105, 266.106, and 266.107;
- (ii) At least 30 days prior to first burning hazardous waste under operating conditions that exceed those established under a current certification of compliance, the owner or operator shall notify the Director and submit the following information:
- (A) EPA facility ID number, and facility name, contact person, telephone number, and address;
- (B) Operating conditions that the owner or operator is seeking to revise and description of the changes in facility design or operation that prompted the need to seek to revise the operating conditions;
- (C) A determination that when operating under the revised operating conditions, the applicable emissions standards of §§266.104, 266.105, 266.106, and 266.107 are not likely to be exceeded. To document this determination, the owner or operator shall submit the applicable information required under paragraph (b)(2) of this section; and
- (D) Complete emissions testing protocol for any pretesting and for a new compliance test to determine compliance with the applicable emissions standards of §\$266.104, 266.105, 266.106, and 266.107 when operating under revised operating conditions. The protocol shall include a schedule of pre-testing and compliance testing. If the owner and operator revises the scheduled date for the compliance test, he/she shall notify the Director in writing at least 30 days prior to the revised date of the compliance test;

- (iii) Conduct a compliance test under the revised operating conditions and the protocol submitted to the Director to determine compliance with the applicable emissions standards of §§266.104, 266.105, 266.106, and 266.107; and
- (iv) Submit a revised certification of compliance under paragraph (c)(4) of this section.
- (d) Periodic Recertifications. The owner or operator must conduct compliance testing and submit to the Director a recertification of compliance under provisions of paragraph (c) of this section within three years from submitting the previous certification or recertification. If the owner or operator seeks to recertify compliance under new operating conditions, he/she must comply with the requirements of paragraph (c)(8) of this section.
- (e) Noncompliance with certification schedule. If the owner or operator does not comply with the interim status compliance schedule provided by paragraphs (b), (c), and (d) of this section, hazardous waste burning must terminate on the date that the deadline is missed, closure activities must begin under paragraph (l) of this section, and hazardous waste burning may not resume except under an operating permit issued under §270.66 of this chapter.
- (f) Start-up and shut-down. Hazardous waste (except waste fed solely as an ingredient under the Tier I (or adjusted Tier I) feed rate limits for metals and chloride/chlorine) must not be fed into the device during start-up and shut-down of the boiler or industrial furnace, unless the device is operating within the conditions of operation specified in the certification of compliance.
- (g) Automatic waste feed cutoff. During the compliance test required by paragraph (c)(3) of this section, and upon certification of compliance under paragraph (c) of this section, a boiler or industrial furnace must be operated with a functioning system that automatically cuts off the hazardous waste feed when the applicable operating conditions specified in paragraphs (c)(1)(i) and (v through xiii) of this section deviate from those established in the certification of compliance. In addition:
- (1) To minimize emissions or organic compounds, the minimum combustion chamber temperature (or the indicator of combustion chamber temperature) that occurred during the compliance test must be maintained while hazardous waste or hazardous waste residues remain in the combustion chamber, with the minimum temperature during the compliance test defined as either:
- (i) If compliance with the combustion chamber temperature limit is based on a hourly rolling average, the minimum temperature during the compliance test is considered to be the average over all runs of the lowest hourly rolling average for each run; or
- (ii) If compliance with the combustion chamber temperature limit is based on an instantaneous temperature measurement, the minimum temperature during the compliance test is considered to be the time-weighted average temperature during all runs of the test; and
- (2) Operating parameters limited by the certification of compliance must continue to be monitored during the cutoff, and the hazardous waste feed shall not be restarted until the levels of those parameters comply with the limits established in the certification of compliance.

- (h) Fugitive emissions. Fugitive emissions must be controlled by:
- (1) Keeping the combustion zone totally sealed against fugitive emissions; or
- (2) Maintaining the combustion zone pressure lower than atmospheric pressure; or
- (3) An alternate means of control that the owner or operator can demonstrate provide fugitive emissions control equivalent to maintenance of combustion zone pressure lower than atmospheric pressure. Support for such demonstration shall be included in the operating record.
- (i) Changes. A boiler or industrial furnace must cease burning hazardous waste when changes in combustion properties, or feed rates of the hazardous waste, other fuels, or industrial furnace feedstocks, or changes in the boiler or industrial furnace design or operating conditions deviate from the limits specified in the certification of compliance.
- (j) Monitoring and Inspections. (1) The owner or operator must monitor and record the following, at a minimum, while burning hazardous waste:
- (i) Feed rates and composition of hazardous waste, other fuels, and industrial furnace feed stocks, and feed rates of ash, metals, and total chloride and chlorine as necessary to ensure conformance with the certification of precompliance or certification of compliance;
- (ii) Carbon monoxide (CO), oxygen, and if applicable, hydrocarbons (HC), on a continuous basis at a common point in the boiler or industrial furnace downstream of the combustion zone and prior to release of stack gases to the atmosphere in accordance with the operating limits specified in the certification of compliance. CO, HC, and oxygen monitors must be installed, operated, and maintained in accordance with methods specified in Methods Manual for Compliance with the BIF Regulations (incorporated by reference, see § 260.11).
- (iii) Upon the request of the Director, sampling and analysis of the hazardous waste (and other fuels and industrial furnace feed stocks as appropriate) and the stack gas emissions must be conducted to verify that the operating conditions established in the certification of precompliance or certification of compliance achieve the applicable standards of §§266.104, 266.105, 266.106, and 266.107.
- (2) The boiler or industrial furnace and associated equipment (pumps, valves, pipes, fuel storage tanks, etc.) must be subjected to thorough visual inspection when they contain hazardous waste, at least daily for leaks, spills, fugitive emissions, and signs of tampering.
- (3) The automatic hazardous waste feed cutoff system and associated alarms must be tested at least once every 7 days when hazardous waste is burned to verify operability, unless the owner or operator can demonstrate that weekly inspections will unduly restrict or upset operations and that less frequent inspections will be adequate. Support for such demonstration shall be included in the operating record. At a minimum, operational testing must be conducted at least once every 30 days.
- (4) These monitoring and inspection data must be recorded and the records must be placed in the operating log.

- (k) Recordkeeping. The owner or operator must keep in the operating record of the facility all information and data required by this section for a period of three years.
- (1) Closure. At closure, the owner or operator must remove all hazardous waste and hazardous waste residues (including, but not limited to, ash, scrubber waters, and scrubber sludges) from the boiler or industrial furnace and must comply with §§265.111-265.115 of this chapter.

(Approved by the Office of Management and Budget under control number \_\_\_\_\_)

## § 266.104 - Standards to control organic emissions.

(a) DRE standard. (1) General. Except as provided in paragraph (a)(3) of this section, a boiler or industrial furnace burning hazardous waste must achieve a destruction and removal efficiency (DRE) of 99.99% for all organic hazardous constituents in the waste feed. To demonstrate conformance with this requirement, 99.99% DRE must be demonstrated during a trial burn for each principal organic hazardous constituent (POHC) designated (under paragraph (a)(2) of this section) in its permit for each waste feed. DRE is determined for each POHC from the following equation:

$$DRE = \begin{bmatrix} 1 - W_{Out} \\ W_{in} \end{bmatrix} \times 100$$

where:

W<sub>in</sub> = Mass feed rate of one principal organic hazardous constituent (POHC) in the hazardous waste fired to the boiler or industrial furnace; and

W<sub>out</sub> = Mass emission rate of the same POHC present in stack gas prior to release to the atmosphere.

- (2) Designation of POHCs. Principal organic hazardous constituents (POHCs) are those compounds for which compliance with the DRE requirements of this section shall be demonstrated in a trial burn in conformance with procedures prescribed in §270.66 of this chapter. One or more POHCs shall be designated by the Director for each waste feed to be burned. POHCs shall be designated based on the degree of difficulty of destruction of the organic constituents in the waste and on their concentrations or mass in the waste feed considering the results of waste analyses submitted with Part B of the permit application. POHCs are most likely to be selected from among those compounds listed in Part 261, Appendix VIII of this chapter that are also present in the normal waste feed. However, if the applicant demonstrates to the Regional Administrator's satisfaction that a compound not listed in Appendix VIII or not present in the normal waste feed is a suitable indicator of compliance with the DRE requirements of this section, that compound may be designated as a POHC. Such POHCs need not be toxic or organic compounds.
- (3) Dioxin-listed waste. A boiler or industrial furnace burning hazardous waste containing (or derived from) EPA Hazardous Wastes Nos. F020, F021, F022, F023, F026, or F027 must achieve a destruction and removal efficiency (DRE) of 99.9999% for each POHC designated (under paragraph (a)(2) of this section) in its permit. This performance must be demonstrated on POHCs that are more difficult to burn than tetra-, penta-, and hexachlorodibenzo-p-dioxins and dibenzofurans. DRE is determined for each

POHC from the equation in paragraph (a) of this section. In addition, the owner or operator of the boiler or industrial furnace must notify the Director of intent to burn EPA Hazardous Waste Nos. F020, F021, F022, F023, F026, or F027.

- (4) Automatic waiver of DRE trial burn. Owners and operators of boilers operated under the special operating requirements provided by § 266.110 are considered to be in compliance with the DRE standard of paragraph (a)(1) of this section and are exempt from the DRE trial burn.
- (5) Low risk waste. Owners and operators of boilers or industrial furnaces that burn hazardous waste in compliance with the requirements of §266.109(a) are considered to be in compliance with the DRE standard of paragraph (a)(1) of this section and are exempt from the DRE trial burn.
- (b) Carbon monoxide standard. (1) Except as provided in paragraph (c) of this section, the stack gas concentration of carbon monoxide (CO) from a boiler or industrial furnace burning hazardous waste cannot exceed 100 ppmv on an hourly rolling average basis (i.e., over any 60 minute period), continuously corrected to 7 percent oxygen, dry gas basis.
- (2) CO and oxygen shall be continuously monitored in conformance with "Performance Specifications for Continuous Emission Monitoring of Carbon Monoxide and Oxygen in Hazardous Waste Incinerators, Boilers, and Industrial Furnaces" in Methods Manual for Compliance with the BIF Regulations (incorporated by reference in §260.11 of this chapter).
- (3) Compliance with the 100 ppmv CO limit must be demonstrated during the trial burn (for new facilities or an interim status facility applying for a permit) or the compliance test (for interim status facilities). To demonstrate compliance, the highest hourly rolling average CO level during any valid run of the trial burn or compliance test must not exceed 100 ppmv.
- (c) Alternative carbon monoxide standard. (1) The stack gas concentration of carbon monoxide (CO) from a boiler or industrial furnace burning hazardous waste may exceed the 100 ppmv limit provided that stack gas concentrations of hydrocarbons (HC) do not exceed 20 ppmv, except as provided by paragraph (f) of this section for certain industrial furnaces.
- (2) HC limits must be established under this section on an hourly rolling average basis (i.e., over any 60 minute period), reported as propane, and continuously corrected to 7 percent oxygen, dry gas basis.
- (3) HC shall be continuously monitored in conformance with "Measurement of Total Hydrocarbons in Stack Gases from Hazardous Waste Incinerators, Boilers, and Industrial Furnaces" in Methods Manual for Compliance with the BIF Regulations (incorporated by reference in §260.11 of this chapter). CO and oxygen shall be continuously monitored in conformance with paragraph (b)(2) of this section.
- (4) The alternative CO standard is established based on CO data during the trial burn (for a new facility) and the compliance test (for an interim status facility). The alternative CO standard is the average over all valid runs of the highest hourly average CO level for each run. The CO limit is implemented on an hourly rolling average basis, and continuously corrected to 7 percent oxygen, dry gas basis.

- (d) Special requirements for furnaces. Owners and operators of industrial furnaces (e.g., kilns, cupolas) that feed hazardous waste for a purpose other than solely as an ingredient (see §266.103(a)(5)(ii)) at any location other than the end where products are normally discharged and where fuels are normally fired must comply with the hydrocarbon limits provided by paragraphs (c) or (f) of this section irrespective of whether stack gas CO concentrations meet the 100 ppmv limit of paragraph (b) of this section.
- (e) Controls for dioxins and furans. Owners and operators of boilers and industrial furnaces that are equipped with a dry particulate matter control device that operates within the temperature range of 450-750°F, and industrial furnaces operating under an alternative hydrocarbon limit established under paragraph (f) of this section must conduct a site-specific risk assessment as follows to demonstrate that emissions of chlorinated dibenzo-p-dioxins and dibenzofurans do not result in an increased lifetime cancer risk to the hypothetical maximum exposed individual (MEI) exceeding 1 in 100,000:
- (1) During the trial burn (for new facilities or an interim status facility applying for a permit) or compliance test (for interim status facilities), determine emission rates of the tetra-octa congeners of chlorinated dibenzo-p-dioxins and dibenzofurans (CDDs/CDFs) using Method 23, "Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans (PCDFs) from Stationary Sources" in Methods Manual for Compliance with the BIF Regulations (incorporated by reference in §260.11).
- (2) Estimate the 2,3,7,8-TCDD toxicity equivalence of the tetra-octa CDDs/CDFs congeners using "Procedures for Estimating the Toxicity Equivalence of Chlorinated Dibenzo-p-Dioxin and Dibenzofuran Congeners" in Methods Manual for Compliance with the BIF Regulations (incorporated by reference in §260.11). Multiply the emission rates of CDD/CDF congeners with a toxicity equivalence greater than zero (see the procedure) by the calculated toxicity equivalence factor to estimate the equivalent emission rate of 2,3,7,8-TCDD.
- (3) Conduct dispersion modeling using methods recommended in Guideline on Air Quality Models, the "Hazardous Waste Combustion Air Quality Screening Procedure" described in Methods Manual for Compliance with the BIF Regulations, or "EPA SCREEN Screening Procedure" as described in Screening Procedures for Estimating Air Quality Impact of Stationary Sources (all three documents are incorporated by reference in §260.11) to predict the maximum annual average off-site ground level concentration of 2,3,7,8-TCDD equivalents determined under paragraph (e)(2) of this section. The maximum annual average on-site concentration must be used when a person resides on-site; and
- (4) The ratio of the predicted maximum annual average ground level concentration of 2,3,7,8-TCDD equivalents to the risk-specific dose for 2,3,7,8-TCDD provided in Appendix V of this part (2.2 X 10<sup>-7</sup>) shall not exceed 1.0.
- (f) Alternative HC limit for furnaces with organic matter in raw material. For industrial furnaces that cannot meet the 20 ppmv HC limit because of organic matter in normal raw material, the Director may establish an alternative HC limit on a case-by-case basis (under a Part B permit proceeding) at a level that ensures that flue gas HC (and CO) concentrations when burning hazardous waste are not greater than when not burning hazardous waste (the baseline HC level) provided that the owner or operator complies with the following requirements. However, cement kilns equipped with a by-pass duct meeting

the requirements of paragraph (g) of this section, are not eligible for an alternative HC limit.

- (1) The owner or operator must demonstrate that the facility is designed and operated to minimize hydrocarbon emissions from fuels and raw materials when the baseline HC (and CO) level is defined. The baseline HC (and CO) level is defined as the average over all valid test runs of the highest hourly rolling average value for each run when the facility does not burn hazardous waste, and produces normal products under normal operating conditions feeding normal feedstocks and fuels. More than one baseline level may be determined if the facility operates under different modes that may generate significantly different HC (and CO) levels;
- (2) The owner or operator must develop an approach to monitor over time changes in the operation of the facility that could reduce the baseline HC level;
  - (3) The owner or operator must conduct emissions testing during the trial burn to:
  - (i) Determine the baseline HC (and CO) level;
- (ii) Demonstrate that, when hazardous waste is burned, HC (and CO) levels do not exceed the baseline level; and
- (iii) Identify the types and concentrations of organic compounds listed in Appendix VIII, Part 261 of this chapter, that are emitted and conducts dispersion modeling to predict the maximum annual average ground level concentration of each organic compound. Onsite ground level concentrations must be considered for this evaluation if a person resides on site.
- (A) Sampling and analysis of organic emissions shall be conducted using procedures prescribed by the Director.
- (B) Dispersion modeling shall be conducted according to procedures provided by paragraph (e)(2) of this section; and
- (iv) Demonstrate that maximum annual average ground level concentrations of the organic compounds identified in paragraph (f)(2)(iii) of this section do not exceed the following levels:
- (A) For the noncarcinogenic compounds listed in Appendix IV of this part, the levels established in Appendix IV;
- (B) For the carcinogenic compounds listed in Appendix V of this part, the sum for all compounds of the ratios of the actual ground level concentration to the level established in Appendix V cannot exceed 1.0. To estimate the health risk from chlorinated dibenzo-p-dioxins and dibenzofuran congeners, use the procedures prescribed by paragraph (e)(3) of this section to estimate the 2,3,7,8-TCDD toxicity equivalence of the congeners.
- (C) For compounds not listed in Appendix IV or V, 0.09 micrograms per cubic meter.
- (4) All hydrocarbon levels specified under this paragraph are to be monitored and reported as specified in paragraphs (c)(1) and (c)(2) of this section.

- (g) Monitoring CO and HC in the by-pass duct of a cement kiln. Cement kilns may comply with the carbon monoxide and hydrocarbon limits provided by paragraphs (b), (c), and (d) of this section by monitoring in the by-pass duct provided that:
- (1) Hazardous waste is fired only into the kiln and not at any location downstream from the kiln exit relative to the direction of gas flow; and
- (2) The by-pass duct diverts a minimum of 10% of kiln off-gas into the duct.(g) Use of emissions test data to demonstrate conformance and establish operating limits: Conformance with the requirements of this section must be demonstrated simultaneously by emissions testing or during separate runs under identical operating conditions. Further, data to demonstrate compliance with the CO and HC limits provided by this section or to establish alternative CO or HC limits provided by this section must be obtained during the time that DRE testing, and where applicable, CDD/CDF testing is being conducted.
- (h) Use of emissions test data to demonstrate compliance and establish operating limits. Compliance with the requirements of this section must be demonstrated simultaneously by emissions testing or during separate runs under identical operating conditions. Further, data to demonstrate compliance with the CO and HC limits of this section or to establish alternative CO or HC limits under this section must be obtained during the time that DRE testing, and where applicable, CDD/CDF testing under paragraph (e) and comprehensive organic emissions testing under paragraph (f) is conducted.
- (i) Enforcement. For the purposes of permit enforcement, compliance with the operating requirements specified in the permit (under § 266.102) will be regarded as compliance with this section. However, evidence that compliance with those permit conditions is insufficient to ensure compliance with the requirements of this section may be "information" justifying modification or revocation and re-issuance of a permit under §270.41 of this chapter.

### § 266.105 Standards to control particulate matter.

- (a) A boiler or industrial furnace burning hazardous waste may not emit particulate matter in excess of 180 milligrams per dry standard cubic meter (0.08 grains per dry standard cubic foot) after correction to a stack gas concentration of 7% oxygen, using procedures prescribed in 40 CFR Part 60, Appendix A, Methods 1 through 5, and Methods Manual for Compliance with the BIF Regulations (incorporated by reference, see §260.11).
- (b) An owner or operator meeting the requirements of \$266.109(b) for the low risk waste exemption is exempt from the particulate matter standard.
- (c) For the purposes of permit enforcement, compliance with the operating requirements specified in the permit (under § 266.102) will be regarded as compliance with this section. However, evidence that compliance with those permit conditions is insufficient to ensure compliance with the requirements of this section may be "information" justifying modification or revocation and re-issuance of a permit under § 270.41 of this chapter.

#### § 266.106 Standards to control metals emissions.

(a) General. The owner or operator must comply with the metals standards provided by paragraphs (b), (c), (d), (e), or (f) of this section for each metal listed in paragraph (b) of this section that is present in the hazardous waste at detectable levels using

analytical procedures specified in <u>Test Methods for Evaluation Solid Waste</u>. <u>Physical/Chemical Methods</u> (SW-846), incorporated by reference in §260.11 of this chapter.

- (b) Tier I feed rate screening limits. Feed rate screening limits for metals are specified in Appendix I of this part as a function of terrain-adjusted effective stack height and terrain and land use in the vicinity of the facility. Criteria for facilities that are not eligible to comply with the screening limits are provided in paragraph (b)(7) of this section.
- (1) Noncarcinogenic metals. The feed rates of antimony, barium, lead, mercury, thallium, and silver in all feed streams, including hazardous waste, fuels, and industrial furnace feed stocks shall not exceed the screening limits specified in Appendix I of this part.
- (i) The feed rate screening limits for antimony, barium, mercury, thallium, and silver are based on either:
  - (A) An hourly rolling average as defined in §266.102(e)(6)(i)(B); or
  - (B) An instantaneous limit not to be exceeded at any time.
  - (ii) The feed rate screening limit for lead is based on one of the following:
  - (A) An hourly rolling average as defined in §266.102(e)(6)(i)(B);
- (B) An averaging period of 2 to 24 hours as defined in §266.102(e)(6)(ii) with an instantaneous feed rate limit not to exceed 10 times the feed rate that would be allowed on an hourly rolling average basis; or
  - (C) An instantaneous limit not to be exceeded at any time.
- (2) Carcinogenic metals. (i) The feed rates of arsenic, cadmium, beryllium, and chromium in all feed streams, including hazardous waste, fuels, and industrial furnace feed stocks shall not exceed values derived from the screening limits specified in Appendix I of this part. The feed rate of each of these metals is limited to a level such that the sum of the ratios of the actual feed rate to the feed rate screening limit specified in Appendix I shall not exceed 1.0, as provided by the following equation:

$$\sum_{i=1}^{n} \frac{AFR(i)}{FRSL(i)} \le 1.0$$

where:

n = number of carcinogenic metals

AFR = actual feed rate to the device for metal "i"

FRSL = feed rate screening limit provided by Appendix I of this part for metal "i".

- (ii) The feed rate screening limits for the carcinogenic metals are based on either:
- (A) An hourly rolling average; or

- (B) An averaging period of 2 to 24 hours with an instantaneous feed rate limit not to exceed 10 times the feed rate that would be allowed on an hourly rolling average basis.
- (3) TESH. (i) The terrain-adjusted effective stack height is determined according to the following equation:

TESH = Ha + H1 - Tr

where:

Ha = Actual physical stack height

H1 = Plume rise as determined from Appendix VI of this part as a function of stack flow rate and stack gas exhaust temperature.

Tr = Terrain rise within five kilometers of the stack.

- (ii) The stack height (Ha) may not exceed good engineering practice as specified in 40 CFR Part 51.100(ii).
- (iii) If the TESH for a particular facility is not listed in the table in the appendices, the nearest lower TESH listed in the table shall be used. If the TESH is four meters or less, a value of four meters shall be used.
- (4) Terrain type. The screening limits are a function of whether the facility is located in noncomplex or complex terrain. A device located where any part of the surrounding terrain within 5 kilometers of the stack equals or exceeds the elevation of the physical stack height (Ha) is considered to be in complex terrain and the screening limits for complex terrain apply. Terrain measurements are to be made from U.S. Geological Survey 7.5-minute topographic maps of the area surrounding the facility.
- (5) Land use. The screening limits are a function of whether the facility is located in an area wher the land use is urban or rural. To determine whether land use in the vicinity of the facility is urban or rural, procedures provided in <u>Methods Manual for Compliance with the BIF Regulations</u> (incorporated by reference, see § 260.11) or <u>Guideline on Air Quality Models</u> (incorporated by reference, see § 260.11) shall be used.
- (6) Multiple stacks. Owners and operators of facilities with more than one on-site stack from a boiler, industrial furnace, incinerator, or other thermal treatment unit subject to controls of metals emissions under a RCRA operating permit or interim status controls must comply with the screening limits for all such units assuming all hazardous waste is fed into the device with the worst-case stack based on dispersion characteristics. The worst-case stack is determined from the following equation as applied to each stack:

K = HVT

where:

K = a parameter accounting for relative influence of stack height and plume rise;

H = physical stack height (meters);

 $V = \text{stack gas flow rate } (m^3/\text{second}); \text{ and }$ 

T = exhaust temperature (°K).

The stack with the lowest value of K is the worst-case stack.

- (7) Criteria for facilities not eligible for screening limits. If any criteria below are met, the Tier I (and Tier II) screening limits do not apply. Owners and operators of such facilities must comply with the Tier III standards provided by paragraph (d) of this section.
  - (i) The device is located in a narrow valley less than one kilometer wide;
- (ii) The device has a stack taller than 20 meters and is located such that the terrain rises to the physical height within one kilometer of the facility;
- (iii) The device has a stack taller than 20 meters and is located within five kilometers of a shoreline of a large body of water such as an ocean or large lake;
- (iv) The physical stack height of any stack is less than 2.5 times the height of any building within five building heights or five projected building widths of the stack and the distance from the stack to the closest boundary is within five building heights or five projected building widths of the associated building; or
- (v) The Director determines that standards based on site-specific dispersion modeling are required.
- (8) Implementation. The feed rate of metals in each feedstream must be monitored to ensure that the feed rate screening limits are not exceeded.
- (c) Tier II emission rate screening limits. Emission rate screening limits are specified in Appendix I as a function of terrain-adjusted effective stack height and terrain and land use in the vicinity of the facility. Criteria for facilities that are not eligible to comply with the screening limits are provided in paragraph (b)(7) of this section.
- (1) Noncarcinogenic metals. The emission rates of antimony, barium, lead, mercury, thallium, and silver shall not exceed the screening limits specified in Appendix I of this part.
- (2) Carcinogenic metals. The emission rates of arsenic, cadmium, beryllium, and chromium shall not exceed values derived from the screening limits specified in Appendix I of this part. The emission rate of each of these metals is limited to a level such that the sum of the ratios of the actual emission rate to the emission rate screening limit specified in Appendix I shall not exceed 1.0, as provided by the following equation:

$$\sum_{i=1}^{n} \underbrace{AER_{(i)}}_{ERSL_{(i)}} \leq 1.0$$

where:

n = number of carcinogenic metals

AER = actual emission rate for metal "i"

ERSL = emission rate screening limit provided by Appendix I of this part for metal
";"

(3) Implementation. The emission rate limits must be implemented by limiting feed rates of the individual metals to levels during the trial burn (for new facilities or an interim status facility applying for a permit) or the compliance test (for interim status facilities).

The feed rate averaging periods are the same as provided by paragraphs (b)(1)(i and ii) and (b)(2)(ii) of this section. The feed rate of metals in each feedstream must be monitored to ensure that the feed rate limits for the feedstreams specified under §§266.102 or 266.103 are not exceeded.

- (4) Definitions and limitations. The definitions and limitations provided by paragraph (b) of this section for the following terms also apply to the Tier II emission rate screening limits provided by paragraph (c) of this section: terrain-adjusted effective stack height, good engineering practice stack height, terrain type, land use, and criteria for facilities not eligible to use the screening limits.
- (5) Multiple stacks. (i) Owners and operators of facilities with more than one onsite stack from a boiler, industrial furnace, incinerator, or other thermal treatment unit subject to controls on metals emissions under a RCRA operating permit or interim status controls must comply with the emissions screening limits for any such stacks assuming all hazardous waste is fed into the device with the worst-case stack based on dispersion characteristics.
- (ii) The worst-case stack is determined by procedures provided in paragraph (b)(6) of this section.
- (iii) For each metal, the total emissions of the metal from those stacks shall not exceed the screening limit for the worst-case stack.
- (d) Tier III site-specific risk assessment. (1) General. Conformance with the Tier III metals controls must be demonstrated by emissions testing to determine the emission rate for each metal, air dispersion modeling to predict the maximum annual average off-site ground level concentration for each metal, and a demonstration that acceptable ambient levels are not exceeded.
- (2) Acceptable ambient levels. Appendices IV and V of this part list the acceptable ambient levels for purposes of this rule. Reference air concentrations (RACs) are listed for the noncarcinogenic metals and 10<sup>-5</sup> risk-specific doses (RSDs) are listed for the carcinogenic metals. The RSD for a metal is the acceptable ambient level for that metal provided that only one of the four carcinogenic metals is emitted. If more than one carcinogenic metal is emitted, the acceptable ambient level for the carcinogenic metals is a fraction of the RSD as described in paragraph (d)(3).
- (3) Carcinogenic metals. For the carcinogenic metals, arsenic, cadmium, beryllium, and chromium, the sum of the ratios of the predicted maximum annual average off-site ground level concentrations (except that on-site concentrations must be considered if a person resides on site) to the risk-specific dose (RSD) for all carcinogenic metals emitted shall not exceed 1.0 as determined by the following equation:
  - $\sum_{i=1}^{n} \frac{\text{Predicted Ambient Concentration (i)}}{\text{Risk-Specific Dose (i)}} \le 1.0$

where: n = number of carcinogenic metals

(4) Noncarcinogenic metals. For the noncarcinogenic metals, the predicted maximum annual average off-site ground level concentration for each metal shall not exceed the reference air concentration (RAC).

- (5) Multiple stacks. Owners and operators of facilities with more than one on-site stack from a boiler, industrial furnace, incinerator, or other thermal treatment unit subject to controls on metals emissions under a RCRA operating permit or interim status controls must conduct emissions testing and dispersion modeling to demonstrate that the aggregate emissions from all such on-site stacks do not result in an exceedance of the acceptable ambient levels.
- (6) Implementation. Under Tier III, the metals controls must be implemented by limiting feed rates of the individual metals to levels during the trial burn (for new facilities or an interim status facility applying for a permit) or the compliance test (for interim status facilities). The feed rate averaging periods are the same as provided by paragraphs (b)(1)(i and ii) and (b)(2)(ii) of this section. The feed rate of metals in each feedstream must be monitored to ensure that the feed rate limits for the feedstreams specified under §\$266.102 or 266.103 are not exceeded.
- (e) Adjusted Tier I feed rate screening limits. The owner or operator may adjust the feed rate screening limits provided by Appendix I of this part to account for site-specific dispersion modeling. Under this approach, the adjusted feed rate screening limit for each metal is determined by back-calculating from the acceptable ambient levels provided by Appendices IV and V of this part using dispersion modeling to determine the maximum allowable emission rate. This emission rate becomes the adjusted Tier I feed rate screening limit. The feed rate screening limits for carcinogenic metals are implemented as prescribed in paragraph (b)(2) of this section.
- (f) Alternative implementation approaches. (1) The Director may approve on a case-by-case basis approaches to implement the Tier II or Tier III metals emission limits provided by paragraphs (c) or (d) of this section alternative to monitoring the feed rate of metals in each feedstream.
- (2) The emission limits provided by paragraph (d) of this section must be determined as follows:
- (i) For each noncarcinogenic metal, by back-calculating from the RAC provided in Appendix IV of this part to determine the allowable emission rate for each metal using the dilution factor for the maximum annual average ground level concentration predicted by dispersion modeling in conformance with paragraph (h) of this section; and
  - (ii) For each carcinogenic metal, by:
- (A) Back-calculating from the RSD provided in Appendix V of this part to determine the allowable emission rate for each metal if that metal were the only carcinogenic metal emitted using the dilution factor for the maximum annual average ground level concentration predicted by dispersion modeling in conformance with paragraph (h) of this section; and
- (B) If more than one carcinogenic metal is emitted, selecting an emission limit for each carcinogenic metal not to exceed the emission rate determined by paragraph (f)(2)(ii)(A) of this section such that the sum for all carcinogenic metals of the ratio of the selected emission limit to the emission rate determined by that paragraph does not exceed 1.0.

- (g) Emissions testing. (1) General. Emissions testing for metals shall be conducted using the Multiple Metals Train as described in Methods Manual for Compliance with the BIF Regulations (incorporated by reference, see § 260.11).
- (2) Hexavalent chromium. Emissions of chromium are assumed to be hexavalent chromium unless the owner or operator conducts emissions testing to determine hexavalent chromium emissions using procedures prescribed in Methods Manual for Compliance with the BIF Regulations (incorporated by reference, see § 260.11).
- (h) Dispersion modeling. Dispersion modeling required under this section shall be conducted according to methods recommended in Guideline on Air Quality Models (Revised), the "Hazardous Waste Combustion Air Quality Screening Procedure" described in Methods Manual for Compliance with the BIF Regulations, or "EPA SCREEN Screening Procedure" as described in Screening Procedures for Estimating Air Quality Impact of Stationary Sources (all three documents are incorporated by reference, see §260.11) to predict the maximum annual average off-site ground level concentration. However, on-site concentrations must be considered when a person resides on-site.
- (i) Enforcement. For the purposes of permit enforcement, compliance with the operating requirements specified in the permit (under § 266.102) will be regarded as compliance with this section. However, evidence that compliance with those permit conditions is insufficient to ensure compliance with the requirements of this section may be "information" justifying modification or revocation and re-issuance of a permit under § 270.41 of this chapter.

# §266.107 Standards to control hydrogen chloride (HCl) and chlorine (Cl<sub>2</sub>) emissions.

- (a) General. The owner or operator must comply with the hydrogen chloride (HCl) and chlorine (Cl<sub>2</sub>) controls provided by paragraphs (b), (c), or (d) of this section.
- (b) Screening limits. (1) Tier I feed rate screening limits. Feed rate screening limits are specified for total chlorine in Appendix II of this part as a function of terrain-adjusted effective stack height and terrain and land use in the vicinity of the facility. The feed rate of total chlorine and chloride, both organic and inorganic, in all feed streams, including hazardous waste, fuels, and industrial furnace feed stocks shall not exceed the levels specified.
- (2) Tier II emission rate screening limits. Emission rate screening limits for HCl and Cl<sub>2</sub> are specified in Appendix III of this part as a function of terrain-adjusted effective stack height and terrain and land use in the vicinity of the facility. The stack emission rates of HCl and Cl<sub>2</sub> shall not exceed the levels specified.
- (3) Definitions and limitations. The definitions and limitations provided by \$266.106(b) for the following terms also apply to the screening limits provided by this paragraph: terrain-adjusted effective stack height, good engineering practice stack height, terrain type, land use, and criteria for facilities not eligible to use the screening limits.
- (4) Multiple stacks. Owners and operators of facilities with more than one on-site stack from a boiler, industrial furnace, incinerator, or other thermal treatment unit subject to controls on HCl or Cl<sub>2</sub> emissions under a RCRA operating permit or interim status controls must comply with the Tier I and Tier II screening limits for those stacks assuming all

hazardous waste is fed into the device with the worst-case stack based on dispersion characteristics.

- (i) The worst-case stack is determined by procedures provided in §266.106(b)(6).
- (ii) Under Tier I, the total feed rate of chlorine and chloride to all subject devices shall not exceed the screening limit for the worst-case stack.
- (iii) Under Tier II, the total emissions of HCl and Cl<sub>2</sub> from all subject stacks shall not exceed the screening limit for the worst-case stack.
- (c) Tier III site-specific risk assessment. (1) General. Conformance with the Tier III controls must be demonstrated by emissions testing to determine the emission rate for HCl and Cl<sub>2</sub>, air dispersion modeling to predict the maximum annual average off-site ground level concentration for each compound, and a demonstration that acceptable ambient levels are not exceeded.
- (2) Acceptable ambient levels. Appendix IV of this part lists the reference air concentrations (RACs) for HCl (7 micrograms per cubic meter) and Cl<sub>2</sub> (0.4 micrograms per cubic meter).
- (3) Multiple stacks. Owners and operators of facilities with more than one on-site stack from a boiler, industrial furnace, incinerator, or other thermal treatment unit subject to controls on HCl or Cl<sub>2</sub> emissions under a RCRA operating permit or interim status controls must conduct emissions testing and dispersion modeling to demonstrate that the aggregate emissions from all such on-site stacks do not result in an exceedance of the acceptable ambient levels for HCl and Cl<sub>2</sub>.
- (d) Averaging periods. The HCl and Cl<sub>2</sub> controls are implemented by limiting the feed rate of total chlorine and chloride in all feedstreams, including hazardous waste, fuels, and industrial furnace feed stocks. Under Tier I, the feed rate of total chloride and chlorine is limited to the Tier I Screening Limits. Under Tier II and Tier III, the feed rate of total chloride and chlorine is limited to the feed rates during the trial burn (for new facilities or an interim status facility applying for a permit) or the compliance test (for interim status facilities). The feed rate limits are based on either:
  - (i) An hourly rolling average as defined in \$266.102(e)(6); or
  - (ii) An instantaneous basis not to be exceeded at any time.
- (e) Adjusted Tier I feed rate screening limits. The owner or operator may adjust the feed rate screening limits provided by Appendix I of this part to account for site-specific dispersion modeling. Under this approach, the adjusted feed rate screening limit is determined by back-calculating from the acceptable ambient level for Cl2 provided by Appendix IV of this part using dispersion modeling to determine the maximum allowable emission rate. This emission rate becomes the adjusted Tier I feed rate screening limit.
- (f) Emissions testing. Emissions testing for HCl and Cl<sub>2</sub> shall be conducted using the procedures described in Methods Manual for Compliance with the BIF Regulations (incorporated by reference, see § 260.11).
- (g) Dispersion modeling. Dispersion modeling shall be conducted according to the provisions of \$266.106(h).

(h) Enforcement. For the purposes of permit enforcement, compliance with the operating requirements specified in the permit (under § 266.102) will be regarded as compliance with this section. However, evidence that compliance with those permit conditions is insufficient to ensure compliance with the requirements of this section may be "information" justifying modification or revocation and re-issuance of a permit under § 270.41 of this chapter.

### § 266.108 Small quantity on-site burner exemption.

- (a) Exempt quantities. Owners and operators of facilities that burn hazardous waste in an on-site boiler or industrial furnace are exempt from the requirements of this section provided that:
- (1) The quantity of hazardous waste burned in a device for a calendar month does not exceed the limits provided in the following table based on the terrain-adjusted effective stack height as defined in § 266.106(b)(3):

### Exempt Quantities for Small Quantity Burner Exemption

Terrain-Adjusted Effective Stack Height of Device (Meters)	Allowable Hazardous Waste Burning Rate (Gallons/Mo.)	Terrain-Adjusted Effective Stack Height of Device (Meters)	Allowable Hazardous Waste Burning Rate (Gallons/Mo.)
0 to 3.9	0	40.0 to 44.9	210
4.0 to 5.9	13	45.0 to 49.9	260
6.0 to 7.9	18	50.0 to 54.9	330
8.0 to 9.9	27	55.0 to 59.9	400
10.0 to 11.9	40	60.0 to 64.9	490
12.0 to 13.9	48	65.0 to 69.9	610
14 .0 to 15.9	59	70.0 to 74.9	680
16.0 to 17.9	69	75.0 to 79.9	760
18.0 to 19.9	76	80.0 to 84.9	850
20.0 to 21.9	84	85.0 to 89.9	960
22.0 to 23.9	93	90.0 to 94.9	1,100
24.0 to 25.9	100	95.0 to 99.9	1,200
26.0 to 27.9	110	100.0 to 104.9	1,300
28.0 to 29.9	130	105.0 to 109.9	1,500
30.0 to 34.9	140	110.0 to 114.9	1,700
35.0 to 39.9	170	115.0 or greater	1,900

- (2) The maximum hazardous waste firing rate does not exceed at any time 1 percent of the total fuel requirements for the device (hazardous waste plus other fuel) on a volume basis;
- (3) The hazardous waste has a minimum heating value of 5,000 Btu/lb, as generated; and
- (4) The hazardous waste fuel does not contain (and is not derived from) EPA Hazardous Waste Nos. F020, F021, F022, F023, F026, or F027.
- (b) Mixing with nonhazardous fuels. If hazardous waste fuel is mixed with a nonhazardous fuel, the quantity of hazardous waste before such mixing is used to comply with paragraph (a).
- (c) Multiple stacks. If an owner or operator burns hazardous waste in more than one on-site boiler or industrial furnace exempt under this section, the quantity limits provided by paragraph (a)(1) of this section are implemented according to the following equation:
  - n Actual Quantity Burned(i)  $\sum_{i=1}^{n}$  Allowable Quantity Burned(i)  $\leq 1.0$

where:

n means the number of stacks:

Actual Quantity Burned means the waste quantity burned per month in device "i";

Allowable Quantity Burned, means the maximum allowable exempt quantity for stack "i" from the table in (a)(1) above.

Note: Hazardous wastes that are subject to the special requirements for small quantity generators under § 261.5 of this chapter may be burned in an off-site device under the exemption provided by § 266.108, but must be included in the quantity determination for the exemption.

- (d) Notification Requirements. The owner or operator of facilities qualifying for the small quantity burner exemption under this section must provide a one-time signed, written notice to EPA indicating the following:
  - (1) The combustion unit is operating as a small quantity burner of hazardous waste;
- (2) The owner and operator are in compliance with the requirements of this section; and
- (3) The maximum quantity of hazardous waste that the facility may burn per month as provided by §266.108(a)(1).
- (e) Recordkeeping requirements. The owner or operator must maintain at the facility for at least three years sufficient records documenting compliance with the hazardous waste quantity, firing rate, and heating value limits of this section. At a

minimum, these records must indicate the quantity of hazardous waste and other fuel burned in each unit per calendar month, and the heating value of the hazardous waste.

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### §266.109 Low risk waste exemption.

- (a) Waiver of DRE standard. The DRE standard of §266.104(a) does not apply if the boiler or industrial furnace is operated in conformance with (a)(1) of this section and the owner or operator demonstrates by procedures prescribed in (a)(2) of this section that the burning will not result in unacceptable adverse health effects.
  - (1) The device shall be operated as follows:
- (i) A minimum of 50 percent of fuel fired to the device shall be fossil fuel, fuels derived from fossil fuel, tall oil, or, if approved by the Director on a case-by-case basis, other nonhazardous fuel with combustion characteristics comparable to fossil fuel. Such fuels are termed "primary fuel" for purposes of this section. (Tall oil is a fuel derived from vegetable and rosin fatty acids.) The 50 percent primary fuel firing rate shall be determined on a total heat or volume input basis, whichever results in the larger volume of primary fuel fired:
- (ii) Primary fuels and hazardous waste fuels shall have a minimum as-fired heating value of 8,000 Btu/lb;
- (iii) The hazardous waste is fired directly into the primary fuel flame zone of the combustion chamber, and
- (iv) The device operates in conformance with the carbon monoxide controls provided by \$266.104(b)(1). Devices subject to the exemption provided by this section are not eligible for the alternative carbon monoxide controls provided by \$266.104(c).
- (2) Procedures to demonstrate that the hazardous waste burning will not pose unacceptable adverse public health effects are as follows:
- (i) Identify and quantify those nonmetal compounds listed in Appendix VIII, Part 261 of this chapter that could reasonably be expected to be present in the hazardous waste. The constituents excluded from analysis must be identified and the basis for their exclusion explained;
- (ii) Calculate reasonable, worst case emission rates for each constituent identified in paragraph (a)(2)(i) of this section by assuming the device achieves 99.9 percent destruction and removal efficiency. That is, assume that 0.1 percent of the mass weight of each constituent fed to the device is emitted.
- (iii) For each constituent identified in paragraph (a)(2)(i) of this section, use emissions dispersion modeling to predict the maximum annual average ground level concentration of the constituent.
- (A) Dispersion modeling shall be conducted using methods specified in §266.106(h).
- (B) Owners and operators of facilities with more than one on-site stack from a boiler or industrial furnace that is exempt under this section must conduct dispersion

modeling of emissions from all stacks exempt under this section to predict ambient levels prescribed by this paragraph.

- (iv) Ground level concentrations of constituents predicted under paragraph (a)(iii) of this section must not exceed the following levels:
- (A) For the noncarcinogenic compounds listed in Appendix IV of this part, the levels established in Appendix IV;
- (B) For the carcinogenic compounds listed in Appendix V of this part, the sum for all constituents of the ratios of the actual ground level concentration to the level established in Appendix V cannot exceed 1.0; and
- (C) For constituents not listed in Appendix IV or V, 0.002 micrograms per cubic meter.
- (b) Waiver of particulate matter standard. The particulate matter standard of §266.105 does not apply if:
  - (1) The DRE standard is waived under paragraph (a) of this section; and
- (2) The owner or operator complies with the Tier I metals feed rate screening limits provided by §266.106(b).

#### §266.110 Waiver of DRE trial burn for boilers.

Boilers that operate under the special operating requirements of this section, and that do not burn hazardous waste containing (or derived from) EPA Hazardous Waste Nos. F020, F021, F022, F023, F026, or F027, are considered to be in conformance with the DRE standard of §266.104(a), and a trial burn to demonstrate DRE is waived. When burning hazardous waste:

- (a) A minimum of 50 percent of fuel fired to the boiler shall be fossil fuel, fuels derived from fossil fuel, tall oil, or, if approved by the Director on a case-by-case basis, other nonhazardous fuel with combustion characteristics comparable to fossil fuel. Such fuels are termed "primary fuel" for purposes of this section. (Tall oil is a fuel derived from vegetable and rosin fatty acids.) The 50 percent primary fuel firing rate shall be determined on a total heat or volume input basis, whichever results in the larger volume of primary fuel fired:
- (b) Boiler load shall not be less than 40 percent. Boiler load is the ratio at any time of the total heat input to the maximum design heat input;
- (c) Primary fuels and hazardous waste fuels shall have a minimum as-fired heating value of 8,000 Btu/lb, and each material fired in a burner where hazardous waste is fired must have a heating value of at least 8,000 Btu/lb, as-fired;
- (d) The device shall operate in conformance with the carbon monoxide standard provided by \$266.104(b)(1). Boilers subject to the waiver of the DRE trial burn provided by this section are not eligible for the alternative carbon monoxide standard provided by \$266.104(c);
- (e) The boiler must be a watertube type boiler that does not feed fuel using a stoker or stoker type mechanism; and

- (f) The hazardous waste shall be fired directly into the primary fuel flame zone of the combustion chamber with an air or steam atomization firing system, mechanical atomization system, or a rotary cup atomization system under the following conditions:
- (1) Viscosity. The viscosity of the hazardous waste fuel as-fired shall not exceed 300 SSU:
- (2) Particle size. When a high pressure air or steam atomizer, low pressure atomizer, or mechanical atomizer is used, 70% of the hazardous waste fuel must pass through a 200 mesh (74 micron) screen, and when a rotary cup atomizer is used, 70% of the hazardous waste must pass through a 100 mesh (150 micron) screen;
- (3) Mechanical atomization systems. Fuel pressure within a mechanical atomization system and fuel flow rate shall be maintained within the design range taking into account the viscosity and volatility of the fuel;
- (4) Rotary cup atomization systems. Fuel flow rate through a rotary cup atomization system must be maintained within the design range taking into account the viscosity and volatility of the fuel.

### § 266.111 Standards for direct transfer.

- (a) Applicability. The regulations in this section apply to owners and operators of boilers and industrial furnaces subject to §§266.102 or 266.103 if hazardous waste is directly transferred from a transport vehicle to a boiler or industrial furnace without the use of a storage unit.
- (b) Definitions. (1) When used in this section, the following terms have the meanings given below:

Direct transfer equipment means any device (including but not limited to, such devices as piping, fittings, flanges, valves, and pumps) that is used to distribute, meter, or control the flow of hazardous waste between a container (i.e., transport vehicle) and a boiler or industrial furnace.

Container means any portable device in which hazardous waste is transported, stored, treated, or otherwise handled, and includes transport vehicles that are containers themselves (e.g., tank trucks, tanker-trailers, and rail tank cars), and containers placed on or in a transport vehicle.

- (2) This section references several requirements provided in Subparts I and J of Parts 264 and 265. For purposes of this section, the term "tank systems" in those referenced requirements means direct transfer equipment as defined in paragraph (b)(1) of this section.
- (c) General operating requirements. (1) No direct transfer of a pumpable hazardous waste shall be conducted from an open-top container to a boiler or industrial furnace.
- (2) Direct transfer equipment used for pumpable hazardous waste shall always be closed, except when necessary to add or remove the waste, and shall not be opened, handled, or stored in a manner that may cause any rupture or leak.

- (3) The direct transfer of hazardous waste to a boiler or industrial furnace shall be conducted so that it does not:
  - (i) Generate extreme heat or pressure, fire, explosion, or violent reaction;
- (ii) Produce uncontrolled toxic mists, fumes, dusts, or gases in sufficient quantities to threaten human health:
- (iii) Produce uncontrolled flammable fumes or gases in sufficient quantities to pose a risk of fire or explosions;
- (iv) Damage the structural integrity of the container or direct transfer equipment containing the waste;
- (v) Adversely affect the capability of the boiler or industrial furnace to meet the standards provided by §§266.104 through 266.107; or
  - (vi) Threaten human health or the environment.
- (4) Hazardous waste shall not be placed in direct transfer equipment if it could cause the equipment or its secondary containment system to rupture, leak, corrode, or otherwise fail.
- (5) The owner or operator of the facility shall use appropriate controls and practices to prevent spills and overflows from the direct transfer equipment or its secondary containment systems. These include at a minimum:
  - (i) Spill prevention controls (e.g., check valves, dry discount couplings); and
- (ii) Automatic waste feed cutoff to use if a leak or spill occurs from the direct transfer equipment.
- (d) Areas where direct transfer vehicles (containers) are located. Applying the definition of container under this section, owners and operators must comply with the following requirements:
  - (1) The containment requirements of §264.175 of this chapter;
- (2) The use and management requirements of Subpart I, Part 265 of this chapter, except for §§ 265.170 and 265.174; and
  - (3) The closure requirements of §264.178 of this chapter.
- (e) Direct transfer equipment. Direct transfer equipment must meet the following requirements:
- (1) Secondary containment. Owners and operators shall comply with the secondary containment requirements of §265.193 of this chapter, except for paragraphs 265.193(a), (d), (e), and (i) as follows:
  - (i) For all new direct transfer equipment, prior to their being put into service; and

- (ii) For existing direct transfer equipment within 2 years after [the effective date of the rule].
- (2) Requirements prior to meeting secondary containment requirements. (i) For existing direct transfer equipment that does not have secondary containment, the owner or operator shall determine whether the equipment is leaking or is unfit for use. The owner or operator shall obtain and keep on file at the facility a written assessment reviewed and certified by a qualified, registered professional engineer in accordance with §270.11(d) of this chapter that attests to the equipment's integrity by [12 months after the effective date of this rule.]
- (ii) This assessment shall determine whether the direct transfer equipment is adequately designed and has sufficient structural strength and compatibility with the waste(s) to be transferred to ensure that it will not collapse, rupture, or fail. At a minimum, this assessment shall consider the following:
- (A) Design standard(s), if available, according to which the direct transfer equipment was constructed;
  - (B) Hazardous characteristics of the waste(s) that have been or will be handled;
  - (C) Existing corrosion protection measures;
- (D) Documented age of the equipment, if available, (otherwise, an estimate of the age); and
- (E) Results of a leak test or other integrity examination such that the effects of temperature variations, vapor pockets, cracks, leaks, corrosion, and erosion are accounted for.
- (iii) If, as a result of the assessment specified above, the direct transfer equipment is found to be leaking or unfit for use, the owner or operator shall comply with the requirements of §§265.196(a) and (b) of this chapter.
- (3) Inspections and recordkeeping. (i) The owner or operator must inspect at least once each operating hour when hazardous waste is being transferred from the transport vehicle (container) to the boiler or industrial furnace:
- (A) Overfill/spill control equipment (e.g., waste-feed cutoff systems, bypass systems, and drainage systems) to ensure that it is in good working order;
- (B) The above ground portions of the direct transfer equipment to detect corrosion, erosion, or releases of waste (e.g., wet spots, dead vegetation); and
- (C) Data gathered from monitoring equipment and leak-detection equipment, (e.g., pressure and temperature gauges) to ensure that the direct transfer equipment is being operated according to its design.
- (ii) The owner or operator must inspect cathodic protection systems, if used, to ensure that they are functioning properly according to the schedule provided by §265.195(b) of this chapter:

- (iii) Records of inspections made under this paragraph shall be maintained in the operating record at the facility, and available for inspection for at least 3 years from the date of the inspection.
- (4) Design and installation of new ancillary equipment. Owners and operators must comply with the requirements of §265.192 of this chapter.
- (5) Response to leaks or spills. Owners and operators must comply with the requirements of §265.196 of this chapter.
- (6) Closure. Owners and operators must comply with the requirements of §265.197 of this chapter, except for § 265.197(c)(2) through (c)(4).

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### § 266.112 Regulation of residues.

A residue derived from the burning or processing of hazardous waste in a boiler or industrial furnace is not excluded from the definition of a hazardous waste under §261.4(b)(4), (7), or (8) unless the device and the owner or operator meet the following requirements:

- (a) The device meets the following criteria:
- (1) Boilers. Boilers must burn coal and at least 50% of the heat input to the boiler must be provided by the coal;
- (2) Ore or mineral furnaces. Industrial furnaces subject to \$261.4(b)(7) must process at least 50% by weight normal, nonhazardous raw materials;
- (3) Cement kilns. Cement kilns must process at least 50% by weight normal cement-production raw materials;
- (b) The owner or operator demonstrates that the hazardous waste does not significantly affect the residue by demonstrating conformance with either of the following criteria:
- (1) Comparison of waste-derived residue with normal residue. The waste-derived residue must not contain Appendix VIII, Part 261 constituents (toxic constituents) that could reasonably be attributable to the hazardous waste at concentrations significantly higher than in residue generated without burning or processing of hazardous waste, using the following procedure. Toxic compounds that could reasonably be attributable to burning or processing the hazardous waste (constituents of concern) include toxic constituents in the hazardous waste, and the 31 organic compounds listed in Appendix VIII of this part that may be generated as products of incomplete combustion. Sampling and analyses shall be in conformance with procedures prescribed in Test Methods for Evaluating Solid Waste. Physical/Chemical Methods, incorporated by reference in §260.11(a) of this chapter.
- (i) Normal residue. Concentrations of toxic constituents of concern in normal residue shall be determined based on analyses of a minimum of 10 composite samples. The upper 95% confidence level about the mean of the concentration in the normal residue shall be considered the statistically-derived concentration in the normal residue. If changes in raw materials or fuels reduce the statistically-derived concentrations of the toxic

constituents of concern in the normal residue, the statistically-derived concentrations must be revised or statistically-derived concentrations of toxic constituents in normal residue must be established for a new mode of operation with the new raw material or fuel. To determine the upper 95% confidence level about the mean of the concentration in the normal residue, the owner or operator shall use statistical procedures prescribed in "Statistical Methodology for Bevill Residue Determinations" in Methods Manual for Compliance with the BIF Regulations, incorporated by reference in §260.11(a) of this chapter.

- (ii) Waste-derived residue. Concentrations of toxic constituents of concern in waste-derived residue shall be determined based on analysis of samples composited over a period of not more than 24 hours. The concentration of a toxic constituent in the waste-derived residue is not considered to be significantly higher than in the normal residue if the concentration in the waste-derived residue does not exceed the concentration established for the normal residue under paragraph (b)(1)(i) of this section; or
- (2) Comparison of waste-derived residue concentrations with health-based limits. (i) Nonmetal constituents. The concentrations of nonmetal toxic constituents of concern (specified in paragraph (b)(1) of this section) in the waste-derived residue must not exceed the health-based levels specified in Appendix VII of this part. If a health-based limit for a constituent of concern is not listed in Appendix VII of this part, then a limit of 0.002 micrograms per kilogram or the level of detection (using analytical procedures prescribed in SW-846), whichever is higher, shall be used; and
- (ii) Metal constituents. The concentration of metals in an extract obtained using the Toxicity Characteristic Leaching Procedure of §261.24 of this chapter must not exceed the levels specified in Appendix VII of this part; and
- (c) Records sufficient to document compliance with the provisions of this section must be retained for a period of three years. At a minimum, the following shall be recorded:
- (1) Levels of constituents in Appendix VIII, Part 261, that are present in wastederived residues;
- (2) If the waste-derived residue is compared with normal residue under paragraph (b)(1) of this section:
- (i) The levels of constituents in Appendix VIII, Part 261, that are present in normal residues; and
- (ii) Data and information, including analyses of samples as necessary, obtained to determine if changes in raw materials or fuels would reduce the concentration of toxic constituents of concern in the normal residue.

# PART 270--EPA ADMINISTERED PERMIT PROGRAMS: THE HAZARDOUS WASTE PERMIT PROGRAM.

VI. In Part 270:

1. The authority citation for Part 270 continues to read as follows:

Authority: Secs. 1006, 2002, 3005, 3007, and 7004 of the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976, as amended (42 U.S.C. 6905, 6912, 6925, 6927, and 6974.

2. Part 270 is amended by adding §270.22 to read as follows:

# §270.22 Specific Part B information requirements for boilers and industrial furnaces burning hazardous waste.

- (a) Trial burns. (1) General. Except as provided below, owners and operators that are subject to the standards to control organic emissions provided by \$266.104 of this chapter, standards to control particulate matter provided by \$266.105 of this chapter, standards to control metals emissions provided by \$266.106 of this chapter, or standards to control hydrogen chloride or chlorine gas emissions provided by \$266.107 of this chapter must conduct a trial burn to demonstrate conformance with those standards and must submit a trial burn plan or the results of a trial burn, including all required determinations, in accordance with \$270.66.
- (i) A trial burn to demonstrate conformance with a particular emission standard may be waived under provisions of §§266.104 through 266.107 of this chapter and paragraphs (a)(2) through (a)(5) of this section; and
- (ii) The owner or operator may submit data in lieu of a trial burn, as prescribed in paragraph (a)(6) of this section.
- (2) Waiver of trial burn for DRE. (i) Boilers operated under special operating requirements. When seeking to be permitted under §\$266.104(a)(4) and 266.110 of this chapter that automatically waive the DRE trial burn, the owner or operator of a boiler must submit documentation that the boiler operates under the special operating requirements provided by \$266.110 of this chapter.
- (ii) Boilers and industrial furnaces burning low risk waste. When seeking to be permitted under the provisions for low risk waste provided by §§266.104(a)(5) and 266.109(a) of this chapter that waive the DRE trial burn, the owner or operator must submit:
- (A) Documentation that the device is operated in conformance with the requirements of §266.109(a)(1) of this chapter;
- (B) Results of analyses of each waste to be burned, documenting the concentrations of nonmetal compounds listed in Appendix VIII of Part 261 of this chapter, except for those constituents that would reasonably not be expected to be in the waste. The constituents excluded from analysis must be identified and the basis for their exclusion explained. The analysis must rely on analytical techniques specified in <u>Test Methods for the Evaluation of Solid Waste. Physical/ Chemical Methods</u> (incorporated by reference, see §260.11).
- (C) Documentation of hazardous waste firing rates and calculations of reasonable, worst-case emission rates of each constituent identified in paragraph (a)(1)(ii)(B) of this section using procedures provided by \$266.109(a)(2)(ii) of this chapter;
- (D) Results of emissions dispersion modeling for emissions identified in paragraphs (a)(2)(ii)(C) of this section using modeling procedures prescribed by §266.106(h) of this chapter. The Director will review the emission modeling conducted by the applicant to determine conformance with these procedures. The Director will either approve the modeling or determine that alternate or supplementary modeling is appropriate.

- (E) Documentation that the maximum annual average ground level concentration of each constituent identified in paragraph (a)(2)(ii)(B) of this section quantified in conformance with paragraph (a)(2)(ii)(D) of this section does not exceed the allowable ambient level established in Appendices IV of V of Part 266. The acceptable ambient concentration for emitted constituents for which a specific Reference Air Concentration has not been established in Appendix IV or Risk-Specific Dose has not been established in Appendix V is 0.09 micrograms per cubic meter, as noted in the footnote to Appendix IV.
- (3) Waiver of trial burn for metals. When seeking to be permitted under the Tier I (or adjusted Tier I) metals feed rate screening limits provided by §266.106(b) and (e) of this chapter that control metals emissions without requiring a trial burn, the owner or operator must submit:
- (i) Documentation of the feed rate of hazardous waste, other fuels, and industrial furnace feed stocks:
- (ii) Documentation of the concentration of each metal controlled by §266.106(b) or (e) of this chapter in the hazardous waste, other fuels, and industrial furnace feedstocks, and calculations of the total feed rate of each metal;
- (iii) Documentation of how the applicant will ensure that the Tier I feed rate screening limits provided by §266.106(b) or (e) of this chapter will not be exceeded during the averaging period provided by that paragraph;
- (iv) Documentation to support the determination of the terrain-adjusted effective stack height, good engineering practice stack height, terrain type, and land use as provided by §266.106(b)(3) through (b)(5) of this chapter;
- (v) Documentation of compliance with the provisions of §266.106(b)(6), if applicable, for facilities with multiple stacks;
- (vi) Documentation that the facility does not fail the criteria provided by \$266.106(b)(7) for eligibility to comply with the screening limits; and
- (vii) Proposed sampling and metals analysis plan for the hazardous waste, other fuels, and industrial furnace feed stocks.
- (4) Waiver of trial burn for particulate matter. When seeking to be permitted under the low risk waste provisions of \$266.109(b) which waives the particulate standard (and trial burn to demonstrate conformance with the particulate standard), applicants must submit documentation supporting conformance with paragraphs (a)(2)(ii) and (a)(3) of this section.
- (5) Waiver of trial burn for HCl and Cl<sub>2</sub>. When seeking to be permitted under the Tier I (or adjusted Tier I) feed rate screening limits for total chloride and chlorine provided by §266.107(b)(1) and (e) of this chapter that control emissions of hydrogen chloride (HCl) and chlorine gas (Cl<sub>2</sub>) without requiring a trial burn, the owner or operator must submit:
- (i) Documentation of the feed rate of hazardous waste, other fuels, and industrial furnace feed stocks;

- (ii) Documentation of the levels of total chloride and chlorine in the hazardous waste, other fuels, and industrial furnace feedstocks, and calculations of the total feed rate of total chloride and chlorine;
- (iii) Documentation of how the applicant will ensure that the Tier I (or adjusted Tier I) feed rate screening limits provided by §266.107(b)(1) or (e) of this chapter will not be exceeded during the averaging period provided by that paragraph;
- (iv) Documentation to support the determination of the terrain-adjusted effective stack height, good engineering practice stack height, terrain type, and land use as provided by §266.107(b)(3) of this chapter;
- (v) Documentation of compliance with the provisions of \$266.107(b)(4), if applicable, for facilities with multiple stacks;
- (vi) Documentation that the facility does not fail the criteria provided by \$266.107(b)(3) for eligibility to comply with the screening limits; and
- (vii) Proposed sampling and analysis plan for total chloride and chlorine for the hazardous waste, other fuels, and industrial furnace feedstocks.
- (6) Data in lieu of a trial burn. The owner or operator may seek an exemption from the trial burn requirements to demonstrate conformance with §\$266.104 through 266.107 of this chapter and §270.66 by providing the information required by §270.66 from previous compliance testing of the device in conformance with §266.103 of this chapter, or from compliance testing or trial or operational burns of similar boilers or industrial furnaces burning similar hazardous wastes under similar conditions. If data from a similar device is used to support a trial burn waiver, the design and operating information required by §270.66 must be provided for both the similar device and the device to which the data is to be applied, and a comparison of the design and operating information must be provided. The Director shall approve a permit application without a trial burn if he finds that the hazardous wastes are sufficiently similar, the devices are sufficiently similar, the operating conditions are sufficiently similar, and the data from other compliance tests, trial burns, or operational burns are adequate to specify (under §266.102 of this chapter) operating conditions that will ensure conformance with §266.102(c) of this chapter. In addition, the following information shall be submitted:

### (i) For a waiver from any trial burn:

- (A) A description and analysis of the hazardous waste to be burned compared with the hazardous waste for which data from compliance testing, or operational or trial burns are provided to support the contention that a trial burn is not needed;
- (B) The design and operating conditions of the boiler or industrial furnace to be used, compared with that for which comparative burn data are available; and
- (C) Such supplemental information as the Director finds necessary to achieve the purposes of this paragraph.
- (ii) For a waiver of the DRE trial burn, the basis for selection of POHCs used in the other trial or operational burns which demonstrate compliance with the DRE performance standard in \$266.104(a) of this chapter. This analysis should specify the constituents in Appendix VIII, Part 261 of this chapter, that the applicant has identified in the hazardous

waste for which a permit is sought, and any differences from the POHCs in the hazardous waste for which burn data are provided.

- (b) Alternative HC limit for industrial furnaces with organic matter in raw materials. Owners and operators of industrial furnaces requesting an alternative HC limit under §266.104(f) of this chapter shall submit the following information at a minimum:
- (1) Documentation that the furnace is designed and operated to minimize HC emissions from fuels and raw materials:
- (2) Documentation of the proposed baseline flue gas HC (and CO) concentration, including data on HC (and CO) levels during tests when the facility produced normal products under normal operating conditions from normal raw materials while burning normal fuels and when not burning hazardous waste;
- (3) Test burn protocol to confirm the baseline HC (and CO) level including information on the type and flow rate of all feedstreams, point of introduction of all feedstreams, total organic carbon content (or other appropriate measure of organic content) of all nonfuel feedstreams, and operating conditions that affect combustion of fuel(s) and destruction of hydrocarbon emissions from nonfuel sources;
  - (4) Trial burn plan to:
- (i) Demonstrate that flue gas HC (and CO) concentrations when burning hazardous waste do not exceed the baseline HC (and CO) level; and
- (ii) Identify the types and concentrations of organic compounds listed in Appendix VIII, Part 261 of this chapter, that are emitted when burning hazardous waste in conformance with procedures prescribed by the Director;
- (5) Implementation plan to monitor over time changes in the operation of the facility that could reduce the baseline HC level and procedures to periodically confirm the baseline HC level; and
- (6) Such other information as the Director finds necessary to achieve the purposes of this paragraph.
- (c) Alternative metals implementation approach. When seeking to be permitted under an alternative metals implementation approach under §266.106(f) of this chapter, the owner or operator must submit documentation specifying how the approach ensures compliance with the metals emissions standards of §266.106(c) or (d) and how the approach can be effectively implemented and monitored. Further, the owner or operator shall provide such other information that the Director finds necessary to achieve the purposes of this paragraph.
- (d) Automatic waste feed cutoff system. Owners and operators shall submit information describing the automatic waste feed cutoff system, including any pre-alarm systems that may be used.
- (e) Direct transfer. Owners and operators that use direct transfer operations to feed hazardous waste from transport vehicles (containers, as defined in §266.111 of this chapter) directly to the boiler or industrial furnace shall submit information supporting conformance with the standards for direct transfer provided by §266.111 of this chapter.

(f) Residues. Owners and operators that claim that their residues are excluded from regulation under the provisions of \$266.112 of this chapter must submit information adequate to demonstrate conformance with those provisions.

(Approved by the Office of Management and Budget under control number \_\_\_\_\_

3. In §270.42, paragraph (g) is revised to read as follows:

§270.42 Permit modifications at the request of the permittee.

\* \* \* \* \*

- (g) Newly regulated wastes and units. (1) The permittee is authorized to continue to manage wastes listed or identified as hazardous under Part 261 of this chapter, or to continue to manage hazardous waste in units newly regulated as hazardous waste management units, if:
- (i) The unit was in existence as a hazardous waste facility with respect to the newly listed or characterized waste or newly regulated waste management unit on the effective date of the final rule listing or identifying the waste, or regulating the unit;
- (ii) The permittee submits a Class 1 modification request on or before the date on which the waste or unit becomes subject to the new requirements;
- (iii) The permittee is in compliance with the applicable standards of 40 CFR Parts 265 and 266 of this chapter;
- (iv) In the case of Classes 2 and 3 modifications, the permittee also submits a complete modification request within 180 days of the effective date of the rule listing or identifying the waste, or subjecting the unit to RCRA Subtitle C management standards;
- (v) In the case of land disposal units, the permittee certifies that each such unit is in compliance with all applicable requirements of Part 265 of this chapter for groundwater monitoring and financial responsibility on the date 12 months after the effective date of the rule identifying or listing the waste as hazardous, or regulating the unit as a hazardous waste management unit. If the owner or operator fails to certify compliance with all these requirements, he or she will lose authority to operate under this section.
- (2) New wastes or units added to a facility's permit under this subsection do not constitute expansions for the purpose of the 25 percent capacity expansion limit for Class 2 modifications.

4. In §270.42, Appendix I is amended by revising Title L, "Incinerators", items 1 through 7 to read as follows:

APPENDIX I TO SECTION 270.42 -- CLASSIFICATION OF PERMIT MODIFICATIONS

<u>Modifications</u>	Class
L. Incinerators, Boilers, and Industrial Furnaces	
1. Changes to increase by more than 25% any of the following limits authorized in the	
permit: A thermal feed rate limit, a feedstream feed rate limit, a chlorine/chloride feed	
rate limit, a metal feed rate limit, or an ash feed rate limit. The Director will require a	
new trial burn to substantiate compliance with the regulatory performance standards unless this demonstration can be made through other means	3
2. Changes to increase by up to 25% any of the following limits authorized in the permit:	3
A thermal feed rate limit, a feedstream feed rate limit, a chlorine/chloride feed rate limit,	
a metal feed rate limit, or an ash feed rate limit. The Director will require a new trial	
burn to substantiate compliance with the regulatory performance standards unless this	
demonstration can be made through other means	2
3. Modification of an incinerator, boiler, or industrial furnace unit by changing the internal	
size or geometry of the primary or secondary combustion units, by adding a primary or	
secondary combustion unit, by substantially changing the design of any component used	
to remove HCl/Cl <sub>2</sub> , metals, or particulate from the combustion gases, or by changing other features of the incinerator, boiler, or industrial furnace that could affect its	
capability to meet the regulatory performance standards. The Director will require a new	
trial burn to substantiate compliance with the regulatory performance standards unless	
this demonstration can be made through other means.	3
4. Modification of an incinerator, boiler, or industrial furnace unit in a manner that would	
not likely affect the capability of the unit to meet the regulatory performance standards	
but which would change the operating conditions or monitoring requirements specified in	
the permit. The Director may require a new trial burn to demonstrate compliance with	_
the regulatory performance standards	2
5. Operating requirements:	
Modification of the limits specified in the permit for minimum or maximum combustion gas temperature, minimum combustion gas residence time, oxygen	
concentration in the secondary combustion chamber, flue gas carbon monoxide and	
hydrocarbon concentration, maximum temperature at the inlet to the particulate matter	
emission control system, or operating parameters for the air pollution control system.	
The Director will require a new trial burn to substantiate compliance with the	
regulatory performance standards unless this demonstration can be made through other	_
means	3
C Description of Management of the Control of the C	
6. Burning different wastes:  a. If the waste contains a POHC that is more difficult to burn than authorized by the	
permit or if burning of the waste requires compliance with different regulatory	
performance standards than specified in the permit. The Director will require a new trial	
burn to substantiate compliance with the regulatory performance standards unless this	
demonstration can be made through other means	3
b. If the waste does not contain a POHC that is more difficult to burn than authorized by	
the permit and if burning of the waste does not require compliance with different	
regulatory performance standards than specified in the permit	2
Note: See §270.42(g) for modification procedures to be used for the management of newly	
listed or identified wastes. 7. Shakedown and trial burn:	
* * *	
b. Authorization of up to an additional 720 hours of waste burning during the shakedown	
period for determining operational readiness after construction, with the prior approval	
of the Director	11
• • •	
8. Substitution of an alternative type of nonhazardous waste fuel that is not specified in the	
permit	1
100 4 100	
<sup>1</sup> Class 1 modifications requiring prior Agency approval.	

5. Part 270 is amended by adding §270.66 to read as follows:

# §270.66 Permits for boilers and industrial furnaces burning hazardous waste.

- (a) General. Owners and operators of new boilers and industrial furnaces (those not operating under the interim status standards of §266.103 of this chapter) are subject to paragraphs (b) through (f) of this section. Boilers and industrial furnaces operating under the interim status standards of §266.103 of this chapter are subject to paragraph (g) of this section.
- (b) Permit operating periods for new boilers and industrial furnaces. A permit for a new boiler or industrial furnace shall specify appropriate conditions for the following operating periods:
- (1) Pretrial burn period. For the period beginning with initial introduction of hazardous waste and ending with initiation of the trial burn, and only for the minimum time required to bring the boiler or industrial furnace to a point of operation readiness to conduct a trial burn, not to exceed 720 hours operating time when burning hazardous waste, the Director must establish in the Pretrial Burn Period of the permit conditions, including but not limited to, allowable hazardous waste feed rates and operating conditions. The Director may extend the duration of this operational period once, for up to 720 additional hours, at the request of the applicant when good cause is shown. The permit may be modified to reflect the extension according to §270.42.
- (i) Applicants must submit a statement, with Part B of the permit application, that suggests the conditions necessary to operate in compliance with the standards of §§266.104 through 266.107 of this chapter during this period. This statement should include, at a minimum, restrictions on the applicable operating requirements identified in §266.102(e) of this chapter.
- (ii) The Director will review this statement and any other relevant information submitted with Part B of the permit application and specify requirements for this period sufficient to meet the performance standards of §§266.104 through 266.107 of this chapter based on his/her engineering judgment.
- (2) Trial burn period. For the duration of the trial burn, the Director must establish conditions in the permit for the purposes of determining feasibility of compliance with the performance standards of §§266.104 through 266.107 of this chapter and determining adequate operating conditions under §266.102(e) of this chapter. Applicants must propose a trial burn plan, prepared under paragraph (c) of this section, to be submitted with Part B of the permit application.
- (3) Post-trial burn period. (i) For the period immediately following completion of the trial burn, and only for the minimum period sufficient to allow sample analysis, data computation, and submission of the trial burn results by the applicant, and review of the trial burn results and modification of the facility permit by the Director to reflect the trial burn results, the Director will establish the operating requirements most likely to ensure compliance with the performance standards of §§266.104 through 266.107 of this chapter based on his engineering judgment.
- (ii) Applicants must submit a statement, with Part B of the application, that identifies the conditions necessary to operate during this period in compliance with the

performance standards of §\$266.104 through 266.107 of this chapter. This statement should include, at a minimum, restrictions on the operating requirements provided by \$266.102(e) of this chapter.

- (iii) The Director will review this statement and any other relevant information submitted with Part B of the permit application and specify requirements for this period sufficient to meet the performance standards of §§266.104 through 266.107 of this chapter based on his/her engineering judgment.
- (4) Final permit period. For the final period of operation, the Director will develop operating requirements in conformance with §266.102(e) of this chapter that reflect conditions in the trial burn plan and are likely to ensure compliance with the performance standards of §\$266.104 through 107 of this chapter. Based on the trial burn results, the Director shall make any necessary modifications to the operating requirements to ensure compliance with the performance standards. The permit modification shall proceed according to §270.42.
- (c) Requirements for trial burn plans. The trial burn plan must include the following information. The Director, in reviewing the trial burn plan, shall evaluate the sufficiency of the information provided and may require the applicant to supplement this information, if necessary, to achieve the purposes of this paragraph:
- (1) An analysis of each feed stream, including hazardous waste, other fuels, and industrial furnace feed stocks, as fired, that includes:
- (i) Heating value, levels of antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, thallium, total chlorine/chloride, and ash;
  - (ii) Viscosity or description of the physical form of the feed stream;
  - (2) An analysis of each hazardous waste, as fired, including:
- (i) An identification of any hazardous organic constituents listed in Appendix VIII, Part 261, of this chapter that are present in the feed stream, except that the applicant need not analyze for constituents listed in Appendix VIII that would reasonably not be expected to be found in the hazardous waste. The constituents excluded from analysis must be identified and the basis for their exclusion explained. The analysis must be conducted in accordance with analytical techniques specified in <u>Test Methods for the Evaluation of Solid Waste. Physical/ Chemical Methods</u> (incorporated by reference, see §270.6), or their equivalent.
- (ii) An approximate quantification of the hazardous constituents identified in the hazardous waste, within the precision produced by the analytical methods specified in <u>Test Methods for the Evaluation of Solid Waste. Physical/Chemical Methods</u> (incorporated by reference, see §270.6), or other equivalent.
- (iii) A description of blending procedures, if applicable, prior to firing the hazardous waste, including a detailed analysis of the hazardous waste prior to blending, an analysis of the material with which the hazardous waste is blended, and blending ratios.
  - (3) A detailed engineering description of the boiler or industrial furnace, including:
  - (i) Manufacturer's name and model number of the boiler or industrial furnace;

- (ii) Type of boiler or industrial furnace;
- (iii) Maximum design capacity in appropriate units;
- (iv) Description of the feed system for the hazardous waste, and, as appropriate, other fuels and industrial furnace feedstocks:
  - (v) Capacity of hazardous waste feed system;
  - (vi) Description of automatic hazardous waste feed cutoff system(s); and
  - (vii) Description of any air pollution control system; and
- (vii) Description of stack gas monitoring and any pollution control monitoring systems.
- (4) A detailed description of sampling and monitoring procedures including sampling and monitoring locations in the system, the equipment to be used, sampling and monitoring frequency, and planned analytical procedures for sample analysis.
- (5) A detailed test schedule for each hazardous waste for which the trial burn is planned, including date(s), duration, quantity of hazardous waste to be burned, and other factors relevant to the Director's decision under paragraph (b)(2) of this section.
- (6) A detailed test protocol, including, for each hazardous waste identified, the ranges of hazardous waste feed rate, and, as appropriate, the feed rates of other fuels and industrial furnace feedstocks, and any other relevant parameters that may affect the ability of the boiler or industrial furnace to meet the performance standards in §§266.104 through 266.107 of this chapter.
- (7) A description of, and planned operating conditions for, any emission control equipment that will be used.
- (8) Procedures for rapidly stopping the hazardous waste feed and controlling emissions in the event of an equipment malfunction.
- (9) Such other information as the Director reasonably finds necessary to determine whether to approve the trial burn plan in light of the purposes of this paragraph and the criteria in paragraph (b)(2) of this section.
- (d) Trial burn procedures. (1) A trial burn must be conducted to demonstrate conformance with the standards of §§266.104 through 266.107 of this chapter under an approved trial burn plan.
  - (2) The Director shall approve a trial burn plan if he/she finds that:
- (i) The trial burn is likely to determine whether the boiler or industrial furnace can meet the performance standards of §\$266.104 through 266.107 of this chapter;
- (ii) The trial burn itself will not present an imminent hazard to human health and the environment;

- (iii) The trial burn will help the Director to determine operating requirements to be specified under §266.102(e) of this chapter; and
- (iv) The information sought in the trial burn cannot reasonably be developed through other means.
- (3) The applicant must submit to the Director a certification that the trial burn has been carried out in accordance with the approved trial burn plan, and must submit the results of all the determinations required in paragraph (c) of this section. This submission shall be made within 90 days of completion of the trial burn, or later if approved by the Director.
- (4) All data collected during any trial burn must be submitted to the Director following completion of the trial burn.
- (5) All submissions required by this paragraph must be certified on behalf of the applicant by the signature of a person authorized to sign a permit application or a report under §270.11.
- (e) Special procedures for DRE trial burns. When a DRE trial burn is required under §266.104(a) of this chapter, the Director will specify (based on the hazardous waste analysis data and other information in the trial burn plan) as trial Principal Organic Hazardous Constituents (POHCs) those compounds for which destruction and removal efficiencies must be calculated during the trial burn. These trial POHCs will be specified by the Director based on information including his/her estimate of the difficulty of destroying the constituents identified in the hazardous waste analysis, their concentrations or mass in the hazardous waste feed, and, for hazardous waste containing or derived from wastes listed in Part 261, Subpart D of this chapter, the hazardous waste organic constituent(s) identified in Appendix VII of that part as the basis for listing.
- (f) Determinations based on trial burn. During each approved trial burn (or as soon after the burn as is practicable), the applicant must make the following determinations:
- (1) A quantitative analysis of the levels of antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, thallium, silver, and chlorine/chloride, in the feed streams (hazardous waste, other fuels, and industrial furnace feedstocks);
  - (2) When a DRE trial burn is required under §266.104(a) of this chapter:
  - (i) A quantitative analysis of the trial POHCs in the hazardous waste feed;
- (ii) A quantitative analysis of the stack gas for the concentration and mass emissions of the trial POHCs; and
- (iii) A computation of destruction and removal efficiency (DRE), in accordance with the DRE formula specified in \$266.104(a) of this chapter;
- (3) When a trial burn for chlorinated dioxins and furans is required under \$266.104(e) of this chapter, a quantitative analysis of the stack gas for the concentration and mass emission rate of the 2,3,7,8-chlorinated tetra-octa congeners of chlorinated dibenzo-p-dioxins and furans, and a computation showing conformance with the emission standard.

- (4) When a trial burn for particulate matter, metals, or HCl/Cl<sub>2</sub> is required under §\$266.105, 266.106(c) or (d), or 266.107(b)(2) or (c) of this chapter, a quantitative analysis of the stack gas for the concentrations and mass emissions of particulate matter, metals, or hydrogen chloride (HCl) and chlorine (Cl<sub>2</sub>), and computations showing conformance with the applicable emission performance standards;
- (5) When a trial burn for DRE, metals, or HCl/Cl<sub>2</sub> is required under §§266.104(a), 266.106(c) or (d), or 266.107(b)(2) or (c) of this chapter, a quantitative analysis of the scrubber water (if any), ash residues, other residues, and products for the purpose of estimating the fate of the trial POHCs, metals, and chlorine/chloride;
  - (6) An identification of sources of fugitive emissions and their means of control;
- (7) A continuous measurement of carbon monoxide (CO), oxygen, and where required, hydrocarbons (HC), in the stack gas; and
- (8) Such other information as the Director may specify as necessary to ensure that the trial burn will determine compliance with the performance standards in §\$266.104 through 266.107 of this chapter and to establish the operating conditions required by \$266.102(e) of this chapter as necessary to meet those performance standards.
- (g) Interim status boilers and industrial furnaces. For the purpose of determining feasibility of compliance with the performance standards of §\$266.104 through 266.107 of this chapter and of determining adequate operating conditions under §266.103 of this chapter, applicants owning or operating existing boilers or industrial furnaces operated under the interim status standards of §266.103 must either prepare and submit a trial burn plan and perform a trial burn in accordance with the requirements of this section or submit other information as specified in §270.22(a)(6). Applicants who submit a trial burn plan and receive approval before submission of the Part B permit application must complete the trial burn and submit the results specified in paragraph (f) of this section with the Part B permit application. If completion of this process conflicts with the date set for submission of the Part B application, the applicant must contact the Director to establish a later date for submission of the Part B application or the trial burn results. If the applicant submits a trial burn plan with Part B of the permit application, the trial burn must be conducted and the results submitted within a time period prior to permit issuance to be specified by the Director.

(Approved by the Office of Management and Budget under control number \_\_\_\_\_)

6. §270.72 is amended by adding paragraphs (a)(6) and (b)(7) to read as follows:

§270.72 Changes during interim status.

- (6) Addition of newly regulated units for the treatment, storage, or disposal of hazardous waste if the owner or operator submits a revised Part A permit application on or before the date on which the unit becomes subject to the new requirements.
  - (b) \* \* \*

(a)

(7) Addition of newly regulated units under paragraph (a)(6) of this section.

7. §270.73 is amended by revising paragraphs (f) and (g) to read as follows:

#### §270.73 Termination of interim status.

- (f) For owners and operators of each incinerator facility which as achieved interim status prior to November 8, 1984, interim status terminates on November 8, 1989, unless the owner or operator of the facility submits a Part B application for a RCRA permit for an incinerator facility by November 8, 1986.
- (g) For owners or operators of any facility (other than a land disposal or an incinerator facility) which as achieved interim status prior to November 8, 1984, interim status terminates on November 8, 1992, unless the owner or operator of the facility submits a Part B application for a RCRA permit for the facility by November 8, 1988.

# PART 271 -- REQUIREMENTS FOR AUTHORIZATION OF STATE HAZARDOUS WASTE PROGRAMS

VII. In Part 271:

1. The authority citation for part 271 continues to read as follows:

Authority: 42 U.S.C. 6905, 6912(a), and 6926.

2. Section 271.1(j) is amended by adding the following entry to Table 1 in chronological order by date of publication in the Federal Register:

### §271.1 Purpose and scope.

\* \* \* \* \* (j) \* \* \*

# TABLE 1. -- REGULATIONS IMPLEMENTING THE HAZARDOUS AND SOLID WASTE AMENDMENTS OF 1984

Promulgation date	Title of regulation	Federal Register reference	Effective date	
December 31, 1990	Burning of Hazardous Waste in Boilers and Industrial Furnaces	[insert page numbers]	June 30, 1991	

### **Appendices**

# Appendix I. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Metals

Table I-A. TIER I AND TIER II FEED RATE AND EMISSIONS SCREENING LIMITS FOR NONCARCINOGENIC METALS FOR FACILITIES IN NONCOMPLEX TERRAIN

Values for Urban Areas

Terrain Adjusted			1			
Eff. Stack Ht. (m)	Antimony (g/hr)	Barium (g/hr)	Lead (g/hr)	Mercury (g/hr)	Silver (g/hr)	Thallium (g/hr)
4	6.0E+01	1.0E+04	1.82+01	6.0E+01_	6.0E+02	6 0E+01
6	6.8E+01	1.1E+04	2.0E+01	6.8E+01	6.8E+02	6.8E+01
8	7.6 <b>E</b> +01	1,32+04	2.3E+01	7.6 <b>E</b> +01	7.6E+02	7.6E+01
10	8.6E+01	1.4E+04	2.62+01	8.6E+01	8.6E+02	8.6E+01
12	9.6E+01	1.7E+04	3.0E+01	9.6E+01	9.6E+02	9.6E+01
14	1.12+02	1.8E+04	3.4E+01	1.1E+02	1.12+03	1.1E+02
16	1.32+02	2.1E+04	3.6E+01	1.3E+02	1.3E+03	1.3E+02
18	1.4E+02	2.42+04	4.3E+01	1.4E+02	1.42+03	1.4E+02
20	1.6E+02	2,7 <b>E</b> +04	4.6E+01	1.5E+02	1.6E+03	1,6E+02
22	1.8E+02	3,0E+04	5.4E+01	1.8E+02	1.82+03	1.8E+02
24	2.0E+02	3.4E+04	6.0E+01	2.0E+02	2.0E+03	2.0E+02
26	2.3E+02	3.9E+04	6.8E+01	2.3E+02	2.32+03	2.3E+02
28	2.5E+02	4.3E+04	7.8E+01	2.5E+02	2.6E+03	2.6E+02
30	3.0E+02	5.0E+04	9.0E+01	3.02+02	3.0E+03	3.0E+02
35	4.0E+02	5 . 6E+04	1.12+02	4.0E+02	4.0E+03	4.0E+02
40	4 . 6E+02	7.8E+04	1.4E+02	4.6E+02	4 . 6E+03	4.6E+02
45	6.0E+02	1,02+05	1.8E+02	6.0E+02	6.0E+03	5.0E+02
· 50	7.8E+02	1.3E+05	2.3E+02	7.8E+02	7.8E+03	7.8E+02
55	9.6E+02	1.7E+05	3.0E+02	9.6E+02	9.6E+03	9.6E+02
60	1.22+03	2.0E+05	3.6E+02	1.2E+03	1.2E+04	1.2E+03
65	1.5E+03	2.5 <b>E</b> +05	4.32+02	1.5E+03	1.5E+04	1.5E+03
70	1.7E+03	2.82+05	5.02+02	1.7E+03	1.7E+04	1.7E+03
75	1.92+03	3.2E+05	5.82+02	1.92+03	1.9E+04	1.9E+03
80	2.22+03	3.6E+05	6.4E+02	2.2E+03	2.2E+04	2.2E+03
85	2.5E+03	4.02+05	7.6E+02	2.5E+03	2.5E+04	2.5E+03
90	2.82+03	4.6Z+05	8.22+02	2.8E+03	2.8E+04	2.8E+03
95	3.22+03	5.4E+05	9.6E+02	3.22+03	3.2E+04	3.2E+03
100	3.62+03	6.0E+05	1.1E+03	3,62+03	3.6E+04	3.6E+03
105	4.0 <b>Z+</b> 03	6.8E+05	1.2E+03	4.02+03	4.0E+04	4.0E+03
110	4 . 6E+03	7.8E+05	1.4E+03	4 . 6E+03	4.6E+04	4.6E+03
115	5.4E+03	8.6Z+05	1.8E+03	5.4E+03	5.42+04	5.4E+03
120	6.0E+03	1.0 <b>Z+0</b> 6	1.8E+03	6.0E+03	6.0Z+04	6.0E+03

# Appendix I. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Metals (Continued)

Table I-B. TIER I AND TIER II FEED RATE AND EMISSIONS SCREENING LIMITS FOR NONCARCINOGENIC METALS FOR FACILITIES IN NONCOMPLEX TERRAIN

Values for Rural Areas

			or Knist Viess			
Terrain Adjusted Eff. Stack Ht. (m)	Antimony (g/hr)	Berium (g/hr)	Lead (g/hr)	Mercury (g/hr)	Silver (g/hr)	Thallium (g/hr)
4	3.1E+01	5.2E+03	9.4E+00	3.1E+01	3.1E+02	3.1E+01
6	3.62+01	6,0 <b>2</b> +03	1,1E+01	3.6 <b>2+</b> 01	3.6E+02	3.6E+01
8	4.0E+01	6.8 <b>E+</b> 03	1.2E+01	4.0 <b>2</b> +01	4.0E+02	4.0E+01
10	4.62+01	7.6E+03	1.42+01	4.5E+01	4.6E+02	4.6E+01
12	5.8E+01	9.6E+03	1.72+01	5.8E+01	5.8E+02	5.8E+01
14	6.82+01	1.1E+04	2.12+01	6.8E+01	6.8E+02	6.8E+01
16	8.62+01	1.4E+04	2.6E+01	8.6E+01	8.6E+02	8.6E+01
18	1.12+02	1.8E+04	3.2E+01	1.1E+02	1.1E+03	1.1E+02
20	1.32+02	2.2E+04	4.0E+01	1.3E+02	1.3E+03	1.3E+02
22	1.7E+02	2.82+04	5.02+01	1.72+02	1.7E+03	1.7E+02
24	2.2E+02	3.6E+04	6.4E+01	2.2E+02	2.2E+03	2.2E+02
26	2.8E+02	4 . 6E+04	8.2E+01	2.62+02	2.6E+03	2.8E+02
28	3.5E+02	5.8E+04	1.02+02	3.52+02	3.5E+03	3.5E+02
30	4.3E+02	7.6E+04	1.32+02	4.3E+02	4.3E+03	4.3E+02
35	7.2E+02	1.2E+05	2.12+02	7.2E+02	7.2 <b>5</b> +03	7.2E+02
. 40	1.1E+03	1.8E+05	3.22+02	1.12+03	1.1E+04	1.1E+03
45	1.5E+03	2.5E+05	4.62+02	1.5E+03	1.5E+04	1.5E+03
50	2.02+03	3.32+05	6.0E+02	2.02+03	2.0E+04	2.0E+03
55	2.6E+03	4.4Z+05	7.8E+02	2.6E+03	2.6E+04	2.6E+03
60	3.4E+03	5.82+05	1.02+03	3.42+03	3.4E+04	3.4E+03
65	4 . 62+03	7.6E+05	1.42+03	4.52+03	4.62+04	4.6E+03
70	5.4E+03	9.0E+05	1.62+03	5.4E+03	5.4E+04	5.4E+03
75	6.4E+03	1.1E+06	1.92+03	6.4E+03	6.4E+04	6,4E+03
80	7.6E+03	1.3E+06	2.3E+03	7.6E+03	7.6E+04	7.6E+03
85	9.4E+03	1.5E+06	2.8E+03	9.4E+03	9.4E+04	9.4E+03
90	1.1E+04	1.8E+06	3.32+03	1.1E+04	1.1E+05	1,1E+04
95	1.3E+04	2.25+06	3.92+03	1.3E+04	1.32+05	1.32+04
100	1.5E+04	2.5 <b>2</b> +06	4.6E+03	1.5E+04	1,5E+05	1.5E+04
105	1.82+04	3.02+06	5.42+03	1.82+04	1.8E+05	1.8E+04
110	2.2E+04	3.6Z+06	6.62+03	2.2 <b>E</b> +04	2.2E+05	2.2E+04
115	2.6E+04	4.4E+06	7.8E+03	2.6E+04	2.6E+05	2.6E+04
120	3.1E+04	5.0 <b>2+</b> 06	9.2E+03	3.1 <b>Z+0</b> 4	3,1 <b>2</b> +05	3.1E+04

### Appendix I. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Metals (Continued)

Table I-C. TIER I AND TIER II FEED RATE AND EMISSIONS SCREENING LIMITS FOR NONCARCINOGENIC METALS FOR FACILITIES IN COMPLEX TERRAIN

Values for Urban and Rural Areas Terrain Adjusted Eff. Stack Rt. (m) Antimony (g/hr) Barium (g/hr) Mercury (g/hr) Silver (g/hr) Lead Thallium (g/hr) (g/hr) 1.4E+01 2.4E+03 4.3E+00 1.4E+01 1.4E+02 1.4E+01 5 2.1E+01 3.5E+03 6.2E+00 2.1E+01 2.1E+02 2 1E+01 3 0E+01 5.0E+03 9.2E+00 3.0E+01 8 3.0E+02 3.0E+01 10 4.3E+01 7.6E+03 1.3E+01 4.3E+01 4.3E+02 4.3E+01 5.4E+01 9.0E+03 1.7E+01 12 5.4E+01 5.4E+02 5 4E+01 14 6.8E+01 1.1E+04 2.0E+01 6.8E+01 6.8E+02 6.8E+01 7.8E+01 1.3E+04 2.4E+01 16 7.8E+01 7.8E+02 7 8E+01 8.5E+01 1.4E+04 2.6E+01 8.6E+01 18 8.6E+02 8.6E+01 20 9.6E+01 1.6E+04 2.9E+01 9.6E+01 9.6E+02 9.6E+01 1.8E+04 1.0E+02 3.2E+01 1.0E+02 1.0E+03 1 0E+02 1.9E+04 24 1.2E+02 3.5E+01 1.2E+02 1.2E+03 1.2E+02 26 1.3E+02 2.2E+04 3.6E+01 1.3E+02 1.3E+03 1.3E+02 1.4E+02 2.4E+04 4.3E+01 1.4E+02 28 1.4E+02 1.4E+03 1.6E+02 2.7E+04 4.6E+01 30 1.6E+02 1.6E+03 1.6E+02 2.0E+02 3.3E+04 5.8E+01 35 2.0E+02 2.0E+03 2.0E+02 2.4E+02 4.0E+04 7.2E+01 2.4E+02 40 2.4E+03 2.4E+02 45 3.0E+02 5.0E+04 9.0E+01 3.0E+02 3.0E+03 3.0E+02 50 3.62+02 5.0E+04 1.1E+02 3.5E+02 3.6E+03 3.6E+02 ' 55 4 . SE+02 7.6E+04 1.4E+02 4 . 6E+02 4.6E+03 4.6E+02 60 5.8E+02 9.4E+04 1.7E+02 5.8E+02 5.8E+03 5.8E+02 6.8E+02 65 1.1E+05 2.1E+02 6.8E+02 6.8E+03 6.8E+02 7.8E+02 70 1.3E+05 2.4E+02 7.8E+02 7.8E+03 7.8E+02 8.6E+02 1.4E+05 2.6E+02 8.6E+02 8.6E+03 8.6E+02 80 9.6E+02 1.6E+05 2.9E+02 9.6E+02 9.6E+03 9.6E+02 85 1.1E+03 1.8E+05 3.3E+02 1.1E+03 1.1E+04 1.1E+03 90 1.2E+03 2.0E+05 3.6E+02 1.2E+03 1.2E+4 1.2E+03 95 1.42+03 2.3E+05 4.0E+02 1.4E+03 1.4E+04 1.4E+03 100 1.5E+03 2.6E+05 4.6E+02 1.5E+03 1.5E+04 1.5E+03 105 1.7E+03 2.8E+05 5.0E+02 1.7E+03 1.7E+04 1.7E+03 110 1.9E+03 3.2E+05 5.8E+02 1.9E+03 1.92+04 1.9E+03

115

120

2.1E+03

2.4E+03

3.6E+05

4.0E+05

6.4E+02

7.2E+02

2.1E+03

2.4E+03

2.1E+04

2.4E+04

2.1E+03

2.4E+03

#### Appendix I. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Metals (Continued)

TIER I AND TIER II FEED RATE AND EMISSIONS SCREENING LIMITS Table I-D. FOR NONCARCINOGENIC METALS FOR FACILITIES IN NONCOMPLEX TERRAIN

Values for Use in Rural Areas Values for Use in Urban Areas Cadmium (g/hr) Chromium (g/hr) Beryllium Cadmium Chromium Arsenic Beryllium Arsenic Terrain Adjusted Eff. Stack Ht. (8/hz) (g/hr) (g/hr) (g/hr) (g/hr) (g/hr) (m) 2.4E-01 5.8E-01 8.6E-02 4.3E-01 1.1E+00 1.7E-0.1 8.2E-01 4.6E-01 2.8E-01 5.6E-01 1.0E-01 5.0E-01 1.3E+00 1.9E-01 9.4E-01 5.4E-01 6 1.1E-01 5.6E-01 3.2E-01 7.6E-01 1.4E+00 2.2E-01 1.1E+00 6.0E-01 8 3.6E-01 8.6E-01 1.3E-01 6.4E-01 1.6E+00 2.4E-01 1.2E+00 6.8E-01 10 4.3E-01 1.1E+00 1.6E-01 7.8E-01 2.7E-01 1 AE+00 1.8E+00 7.6E-01 12 1.5E+00 5.4E-01 1.3E+00 2.0E-01 9.6E-01 2.1E+00 3.1E-01 8.6E-01 14 1.7E+00 6.8E-01 1.6E+00 2.4E-01 1.2E+00 3 . 5E-01 2.3E+00 9.6E-01 15 2.0E+00 3.0E-01 1.5E+00 4.0E-01 2.0E+00 8.2E-01 2.5E+00 1.1E+00 18 2.2E+00 1.0E+00 2.5E+00 3.7E-01 1.9E+00 4.4E-01 1.2E+00 3.0E+00 20 3.2E+00 4.8E-01 1.3E+00 2.4E+00 5.0E-01 2.5E+00 1.4E+00 3.4E+00 22 1.7E+00 4.0E+00 6.0E-01 3.0E+00 2.8E+00 3.9E+00 5.8E-01 24 1.6E+00 2.1E+00 5.0E+00 7.6E-01 3.9E+00 4.3E+00 6.4E-01 3,2E+00 26 1.8E+00 5.0E+00-2.7E+00 6.4E+00 9.8E-01 4.8E+00 7.2E-01 3.6E+00 2.0E+00 28 6.2E+00 3.5E+00 8.2E+00 1.2E+00 4.0E+00 30 2.3E+00 5.4E+00 8.2E-01 9.6E+00 1.9E+00 5.4E+00 5.4E+00 1.3E+01 35 3 0E+00 5.8E+00 1.0E+00 8.2E+00 2.0E+01 3.0E+00 1.5E+01 1.3E+00 6.8E+00 9.0E+00 40 3.6E+00 2.1E+01 1.1E+01 2.8E+01 4.2E+00 8.6E+00 4.6E+00 1.1E+01 1.72+00 45 3.7E+01 5.4E+00 2.8E+01 2.2E+00 1.1E+01 1.5E+01 1.4E+01 6.0E+00 50 5.0E+01 7.2E+00 3.6E+01 2.0E+01 1.8E+01 2.7E+00 1.4E+01 55 7.6E+00 9.6E+00 4.8E+01 2.2E+01 3.4E+00 1.7E+01 2.7E+01 6.4E+01 60 9.4E+00 3.6E+01 8 SE+01 1.3E+01 6.4E+01 2.1E+01 2.8E+01 4.2E+00 1.1E+01 65 7.6E+01 4.6E+00 2.4E+01 4.3E+01 1.0E+02 1.5E+01 3.1E+01 1.3E+01 70 1.2E+02 1.8E+01 9.0E+01 5.0E+01 2.7E+01 3.62+01 5.4E+00 75 1.5E+01 2.2E+01 1.1E+02 1.4E+02 3.0E+01 6.0E+01 1.7E+01 4.0E+01 6.0E+00 80 1.3E+02 3.4E+01 7.2E+01 1.7E+02 2.6E+01 6.8E+00 4 . SE+01 85 1.9E+01 3.0E+01 1.5E+02 2.0E+02 8.6E+01 3.9E+01 90 2.2E+01 5.0E+01 7.8E+00 1.8E+02 3.6E+01 1.0E+02 2.4E+02 5.8E+01 9.0E+00 4.4E+01 95 2.5E+01 4.3E+01 2.2E+02 1.2E+02 2.9E+02 5.0E+01 1.0E+01 100 2.8E+01 6.8E+01 2.6E+02 5.0E+01 3.4E+02 5.6E+01 1.4E+02 7.6E+01 1.1E+01 3.2E+01 105 1.7E+02 4.0E+02 5.0E+01 3.0E+02 8.6Z+01 1.3E+01 6.4E+01 3.6E+01 110 3.6E+02 7.2E+01 7.2E+01 2.0E+02 4.82+02 1.5E+01 9.6E+01 4.0E+01 115 4.3E+02

2.4E+02

8.2E+01

1.1E+02

4.6Z+01

120

1.7E+01

5.8E+02

8.6E+01

# Appendix I. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Metals (Continued)

Table I-E. TIER I AND TIER II FEED RATE AND EMISSIONS SCREENING LIMITS FOR CARCINOGENIC METALS FOR FACILITIES IN COMPLEX TERRAIN

Values for Use in Urban and Rural Areas

	V21465 101 0.	e in Urban and Rura.	71.485	
Terrain Adjusted Eff. Stack Ht. (m)	Arsenic (g/hr)	Cadmium (g/hr)	Chromium (g/hr)	Beryllium (g/hr)
4	1,1E-01	2.6E-01	4.0E-02	2.0E-01
6	1.6E-01	3.9E-01	5.8E-02	2.9E-01
8	2.4E-01	5.8E-01	8.6E-02	4.3E-01
10	3.5E-01	8.2E-01	1.3E-01	6.ZE-01
12	4.3-01	1.0E+00	1.5E-01	7.6E-01
14	5.0E-01	1.3E+00	1.9E-01	9.4E-01
16	6,0E-01	1.4E+00	2.2E-01	1.1E+00
18	6,8E-01	1.6E+00	2.42-01	1.2E+00
20	7.6E-01	1.8E+00	2.7E-01	1.3E+00
22	8.2E-01	1.9E+00	3.0E-01	1.5E+00.
24	9.02-01	2.1E+00	3.3E-01	1.6E+00
26	1.0E+00	2.4E+00	3.6E-01	1.8E+00
28	1,1E+00	2.7E+00	4.0E-01	2.0E+00
30	1.2E+00	3.0E+00	4.4E-01	2.2E+00
35	1,5E+00	3.7E+00	5.4E-01	2.7E+00
40	1.9E+00	4.6E+00	6.8E-01	3.4E+00
45	2.4E+00	5.4E+00	8.4E-01	4 . 2E+00
50	2,92+00	6.8E+00	1.0E+00	5.0E+00 ·
55	3 , 5E+00	8.4E+00	1.3E+00	6.4E+00
60	4 , 3E+00	1.02+01	1.5E+00	7.8E+00
65	5, 4E+00	1.3E+01	1.9E+00	9.6E+00
70	6,0 <b>E+00</b>	1.4E+01	2.2E+00	1.1E+01
75	6,8E+00	1.62+01	2.4E+00	1.2E+01
80	7.6E+00	1.82+01	2.7E+00	1.3E+01
85	8,2E+00	2.0E+01	3.02+00	1.5E+01
90	9,4E+00	2.32+01	3.4E+00	1.7E+01
95	1,0E+01	2.5E+01	4.0E+00	1.9E+01
100	1,22+01	2.8E+01	4.3E+00	2.1E+01
105	1,32+01	3.2E+01	4 . 8Z+00	2.4E+01
110	1,5E+01	3.5E+01	5.4+00	2.7E+01
115	1.7E+01	4.0E+01	6.02+00	3.0E+01
120	1.92+01	4.4E+01	6.4E+00	3.3E+01

TIER I FEED RATE SCREENING LIMITS FOR CHLORINE FOR FACILITIES IN NONCOMPLEX AND COMPLEX TERRAIN

Terrain-adjusted	Nonco	plex	Complex
effective stack height (m)	Urban (lb/hr)	Rural (lb/hr)	(lb/hr)
4 6 8 10 12 14 16 18 20 22 24 26 28 33 35 40 45 50 55 60 65 70 75 80 85 90 90 105	1.8E-02 2.0E-02 2.2E-02 2.5E-02 2.9E-02 3.3E-02 4.1E-02 4.7E-02 6.0E-02 6.8E-02 7.6E-02 1.2E-01 1.4E-01 1.4E-01 1.4E-01 1.5.6E-01 2.9E-01 3.6E-01 5.6E-01 6.3E-01 7.3E-01 8.3E-01 7.3E-01 8.3E-01 7.3E-01 8.3E-01	9.2E-03 1.0E-02 1.2E-02 1.4E-02 1.7E-02 2.0E-02 2.5E-02 3.2E-02 6.3E-02 6.3E-02 1.0E-01 1.3E-01 2.1E-01 3.2E-01 4.4E-01 5.8E-01 7.7E-01 1.0E+00 1.6E+00 1.6E+00 1.9E+00 2.2E+00 2.8E+00 3.8E+00 3.8E+00 5.4E+00	4.1E-03 6.1E-03 9.0E-03 1.3E-02 1.6E-02 2.0E-02 2.5E-02 3.1E-02 3.5E-02 4.7E-02 5.8E-02 4.7E-02 5.8E-02 1.1E-01 1.4E-01 1.7E-01 2.0E-01 2.3E-01 2.5E-01 2.5E-01 2.0E-01 3.6E-01 4.0E-01 4.4E-01 5.0E-01

TIER II EMISSIONS SCREENING LIMITS FOR C12 AND HC1 IN NONCOMPLEX TERRAIN

Terrain-adjusted effective stack		for use in areas	Values for use in rural areas	
height (m)	Cl <sub>2</sub> (g/sec)	HC1 (g/sec)	Cl <sub>2</sub> (g/sec)	HCl (g/sec)
46 8 10 114 16 18 20 22 24 28 30 35 45 55 65 77 85 90 91 105 110 115 120	2.3E-03 2.5E-03 3.2E-03 3.2E-03 4.1E-03 4.7E-03 5.9E-03 6.7E-03 7.6E-03 1.1E-02 1.5E-02 1.5E-02 2.3E-02 2.9E-02 3.6E-02 4.5E-02 4.5E-02 4.5E-02 1.2E-01 1.2E-01 1.3E-01 1.5E-01 1.2E-01 1.3E-01 1.3E-01 2.3E-01	4.0E-01 4.4E-01 4.9E-01 5.6E-01 6.3E-01 7.2E-01 8.2E-01 9.1E-01 1.0E+00 1.3E+00 1.5E+00 1.7E+00 1.7E+00 2.6E+00 3.0E+00 4.0E+00 5.1E+00 6.3E+00 7.9E+00 9.6E+00 1.1E+01 1.2E+01 1.4E+01 1.6E+01 1.6E+01 2.6E+01 3.0E+01 4.0E+01 4.0E+01 4.0E+01 4.0E+01	1.2E-03 1.3E-03 1.5E-03 1.7E-03 2.1E-03 2.5E-03 4.0E-03 4.9E-03 6.3E-03 8.0E-03 1.0E-02 1.3E-02 1.6E-02 2.7E-02 4.0E-02 7.3E-02 1.7E-01 2.0E-01 2.4E-01 2.4E-01 2.5E-01 4.8E-01 3.5E-01 4.8E-01 5.7E-01 6.8E-01 8.1E-01 1.1E+00	2.0E-01 2.3E-01 3.0E-01 3.7E-01 4.4E-01 5.6E-01 1.1E+00 1.4E+00 1.4E+00 1.8E+00 2.3E+00 4.7E+00 7.0E+00 9.8E+00 1.7E+01 3.5E+01 1.7E+01 3.5E+01 4.2E+01 4.9E+01 6.1E+01 7.0E+01 8.4E+02 1.2E+02 1.2E+02 1.7E+02 2.0E+02

TIER II EMISSIONS SCREENING LIMITS FOR Cl2 AND HC1 IN COMPLEX TERRAL:

Terrain-adjusted effective stack height (m)	Values for and ru	use in urban ral areas
uergac (m)	Cl <sub>2</sub> (g/sec)	HCl (g/sec)
4 6 8 10 12 14 16 18 20 22 24 26 28 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 115 120	5.2E-04 7.7E-03 1.6E-03 2.0E-03 2.5E-03 3.2E-03 3.2E-03 3.4E-03 4.8E-03 5.3E-03 5.3E-03 7.3E-03 1.1E-02 1.7E-02 2.1E-02 2.5E-02 2.5E-02 2.5E-02 2.5E-02 2.5E-02 2.5E-02 3.6E-02 4.0E-02 4.5E-02 5.1E-02 7.1E-02 7.1E-02 7.9E-02 8.9E-02	9.1E-02 1.4E-01 2.0E-01 3.5E-01 4.4E-01 5.1E-01 5.6E-01 6.8E-01 7.7E-01 8.4E-01 9.3E-01 1.0E+00 1.3E+00 1.5E+00 1.6E+00 3.7E+00 3.7E+00 3.7E+00 5.1E+00 5.1E+00 5.1E+00 7.0E+00 7.9E+00 7.9E+00 9.8E+00 1.1E+01 1.2E+01 1.4E+01 1.6E+01

Appendix IV. - Reference Air Concentrations\*

Constituent	CAS No.	RAC (ug/m <sup>3</sup> )
Acetaldehyde	. 75-07-0	10
Acetonitrile		
Acetophenone	. 98-86-2	100
Acrolein	. 107-02-8	20
Aldicarb	. 116-06-3	• 1
Aluminum Phosphide	.20859-73-8	0.3
Allyl Alcohol		5
Antimony	. 7440-36-0	0.3
Barium		50
Barium Cyanide	. 542-62-1	50
Bromomethane		0.8
Calcium Cyanide		30
Carbon Disulfide		200
Chloral	. 75-87-6	2
Chlorine (free)		0.4
2-Chloro-1,3-butadiene		3
Chromium III		1000
Copper Cyanide	. 544-92-3	5
Cresols		50-
Cumene		1
Cyanide (free)	. 57-12-15	20
Cyanogen	. 460-19-5	30
Cyanogen Bromide		80
Di-n-butyl Phthalate		100
o-Dichlorobenzene		10
p-Dichlorobenzene	. 106-46-7	10
Dichlorodifluoromethane.		200
2,4-Dichlorophenol	. 120-83-2	3
Diethyl Phthalate	. 84-66-2	800
Dimethoate	. 60-51-5	0.8
2,4-Dinitrophenol	. 51,-28-5	2
Dinoseb	. 88-85-7	0.9
Diphenylamine		20
Endosulfan	. 115-29-7	0.05
Endrin	. 72-20-8	0.3
Fluorine		50
Formic Acid		2000
Glycidyaldehyde		0.3
Hexachlorocyclopentadier		5
Hexachlorophene		0.3
Hydrocyanic Acid		20
Hydrogen Chloride		7
Hydrogen Sulfide		3
Isobutyl Alcohol		300
Lead		0.09
Maleic Anyhdride	. 108-31-6	
Mercury	. 7439-97-6	0.3
Methacrylonitrile	. 126-98-7	0.1

Constituent	CAS No.	RAC (ug/m³)
	1/750 77 6	
Methomyl		
Methoxychlor		
Methyl Chlorocarbonate.		
Methyl Ethyl Ketone		
Methyl Parathion		
Nickel Cyanide		
Nitric Oxide		
Nitrobenzene		
Pentachlorobenzene		
Pentachlorophenol		
Phenol		
M-Phenylenediamine		5
Phenylmercuric Acetate.		
Phosphine		
Phthalic Anhydride		
Potassium Cyanide		
Potassium Silver Cyanide		
Pyridine		1
Selenious Acid		3·
Selenourea		5
Silver		3
Silver Cyanide	506-64-9	
Sodium Cyanide		. 30
Strychnine	57-24-9	0.3
1,2,4,5-Tetrachlorobenze	ene 95-94-3	0.3
2,3,4,6-Tetrachloropheno	58-90-2	30
Tetraethyl Lead	78-00-2	0.0001
Tetrahydrofuran	109-99-9	10
Thallic Oxide		0.3
Thallium	7440-28-0	0.5
Thallium (I) Acetate	563-68-8	0.5
Thallium (I) Carbonate	. 6533-73-9	0.3
Thallium (I) Chloride	. 7791-12-0	0.3
Thallium (I) Nitrate	10102-45-1	0.5
Thallium Selenite	12039 - 52 - 0	0.5
Thallium (I) Sulfate	7446-18-6	0.075
Thiram	137-26-8	5
Toluene	108-88-3	300
1,2,4-Trichlorobenzene.	120-82-1	20
Trichloromonofluorometha		300
2,4,5-Trichlorophenol		100
Vanadium Pentoxide		20
Warfarin		0.3
Xylenes		80
Zinc Cyanide		50
Zinc Phosphide		0.3
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<sup>\*</sup> The RAC for other Appendix VIII Part 261 constituents not listed herein or in Appendix 4. of this Part is  $0.09 \text{ ug/m}^3$ .

Appendix V. - Risk Specific Doses (10<sup>-5</sup>)

Constituent	CAS No.	Unit risk (m3/ug)	RsD (ug/m3)
Acrylamide	79-06-1	1.3E-03	7.7E-03
Acrylonitrile	107-13-1	6.8E-05	1.5E-01
Aldrin	309-00-2	4.9E-03	2.0E-03
Aniline	62-53-3	7.4E-06	1.4E+00
Arsenic	7440-38-2	4.3E-03	2.3E-03
Benz(a)anthracene	56-55-3	8.9E-04	1.1E-02
Benxene	71-43-2	8.3E-06	1.2E+00
Benzidine	92-87-5	6.7E-02	1.5E-04
Benzo(a)pyrene	50-32-8	3.3E-03	3.0E-03
Beryllium	7440-41-7	2.4E-03	4.2E-03
Bis(2-chloroethyl)ether	111-44-4	3.3E-04	3.0E-02
Bis(chloromethyl)ether.	542-88-1	6.2E-02	1.6E-04
Bis(2-ethylhexyl)-			
phthalate	117-81-7	2.4E-07	4.2E+01
1,3-Butadiene	106-99-0	2.8E-04	3.6E-02
Cadmium	7440-43-9	1.8E-03	5.6E-03
Carbon Tetrachloride	56-23-5	1.5E-05	6.7E-01
Chlordane	57-74-9	3.7E-04	2.7E-02
Chloroform	67-66-3	2.3E-05	4.3E-01
Chloromethane	74-87-3	3.6E-06	2.8E+00
Chromium VI	7440-47-3	1.2E-02	8.3E-04
DDT	50-29-3	9.7E-05	1.0E-01
Dibenz(a,h)anthracene	53-70-3	1.4E-02	7.1E-04
1,2-Dibromo-3-			
chloropropane	96-12-8	6.3E-03	1.6E-03
1,2-Dibromoehtane	106-93-4	2.2E-04	4.5E-02
1,1-Dichloroethane	75-34-3	2.6E-05	3.8E-01
1,2-Dichloroethane	107-06-2	2.6E-05	3.8E-01
1,1-Dichloroethylene	75-35-4	5.0E-05	2.0E-01
1,3-Dichloropropene	542-75-6	3.5E-01	2.9E-05
Dieldrin	60-57-1	4.6E-03	2.2E-03
Diethylstilbestrol	56-53-1	1.4E-01	7.1E-05
Dimethylnitrosamine	62-75-9	1.4E-02	7.1E-04
2,4-Dinitrotoluene	121-14-2	8.8E-05	1.1E-01
1,2-Diphenylhydrazine	122-66-7 123-91-1	2.2E-04	4.5E-02 7.1E+00
1,4-Dioxane	106-89-8	1.4E-06 1.2E-06	8.3E+00
Epichlorohydrin Ethylene Oxide	75-21-8	1.0E-04	1.0E-01
Ethylene Dibromide	106-93-4	2.2E-04	4.5E-02
Formaldehyde	50-00-0	1.3E-05	7.7E-01
Heptachlor	76-44-8	1.3E-03	7.7E-03
Heptachlor Eposide	1024-57-3	2.6E-03	3.8E-03
Hexachlorobenzene	118-74-1	4.9E-04	2.0E-02
Hexachlorobutadiene	87-68-3	2.0E-05	5.0E-01
	<del>-</del>	- · · - <del>- · · ·</del>	- · - <b>- · · ·</b>

# Appendix V. (Continued)

Constituent	CAS No.	Unit risk (m3/ug)	RsD (ug/m3)
Alpha-hexachloro-			
cyclohexane	319-84-6	1.8E-03	5.6E-03
Beta-hexachloro-			3.02 03
cyclohexane	319-85-7	5.3E-04	1.9E-02
Gamma-hexachloro-			
cyclohexane	58-89-9	3.8E-04	2.6E-02
Hexachlorocyclo-			
hexane, Technical.		5.1E-04	2.0E-02
Hexachlorodibenxo-p-			
dioxin(1,2 Mixture)		1.3E+00	7.7E-06
Hexachloroethane	67-72-1	4.0E-06	2.5E+00
Hydrazine	302-01-2	2.9E-03	3.4E-03
Hydrazine Sulfate	302-01-2	2.9E-03	3.4E-03
3-Methylcholanthrene	56-49 <i>-</i> 5	2.7E-03	3.7E-03
Methyl Hydrazine	60-34-4	3.1E-04	3.2E-02
Methylene Chloride	75-09-2	4.1E-06	2.4E+00
4,4'-Methylene-bis-2-			
chloroaniline	101-14-4	4.7E-05	2.1E-01
Nickel	7440-02-0	2.4E-04	4.2E-02
Nickel Refinery Dust	7440-02-0	2.4E-04	4.2E-02
Nickel Subsulfide	12035-72-2	4.8E-04	2.1E-02
2-Nitropropane	79-46-9	2.7E-02	3.7E-04
N-Nitroso-n-butylamine.	924-16-3	1.6E-03	6.3E-03
N-Nitroso-n-methylurea.	684-93-5	8.6E-02	1.2E-04
N-Nitrosodiethylamine	55-18-5	4.3E-02	2.3E-04
N-Nitrosopyrrolidine	930-55-2	6.1E-04	1.6E-02
Pentachloronitrobenzene	82-68-8	7.3E-05	1.4E-01
PCBs	1336-36-3	1.2E-03	8.3E-03
Pronamide	23950-58-5	4.6E-06	2.2E+00
Reserpine	50-55-5	3.0E-03	3.3E-03
2,3,7,8-Tetrachloro-	13/4 01 4		0 07 07
dibenzo-p-dioxin	1746-01-6	4.5E+01	2.2E-07
1,1,2,2-Tetrachloroethane		5.8E-05	1.7E-01
Tetrachloroethylene	127-18-4	4.8E-07	2.1E+01
Thiourea	62-56-6 79-00-5	5.5E-04	1.8E-02
1,1,2-Trichloroethane		1.6E-05	6.3E-01 7.7E+00
Trichloroethylene	79-01-6	1.3E-06	
2,4,6-Trichlorophenol	88-06-2 8001-35-2	5.7E-06 3.2E-04	1.8E+00 3.1E-02
Toxaphene	75-01-4	7.1E-06	1.4E+00
Vinyl Chloride	13-01-4	/. TE-00	I. OLTUU

# ESTIMATED PLUME RISE (H1, IN METERS) BASED ON STACK EXIT FLOW RATE AND GAS TEMPERATURE

	Exhaust Temperature (K*)										
Flow Rate (m3/s)	<325	325- 349	350- 399	400 - 449	450- 499	500 - 599	600 - 699	700- 799	800 - 999	1000 - 1499	>1499
<0.5	0	0	0	0	0	0	0	0	0	0	0
0.5-0.9	Ŏ	Ŏ	Ō	0	0	0	0	0	1	1	1
1.0-1.9	Ŏ	Ō	0	0	1	1	2	3	3	3	4
2.0-2.9	Ó	0	1	3	4	4	6	6	7	8	9
3.0-3.9	0	1	2	5	6	7	9	10	11	12	13
4.0-4.9	1	2	4	6	8	10	12	13	14	15	17
5.0-7.4	2	3	5	8	10	12	14	16	17	19	21
7.5-9.9	3	5	8	12	15	17	20	22	22	23	24
10.0-12.4	4	6	10	15	19	21	23	24	25	26	· 27
12.5-14.9	4	7	12	18	22	23	25	26	27	28	29
15.0-19.9	5	8	13	20	23	24	26	27	28	29	31 34 36 39 41
20.0-24.9	6	10	17	23	25	27	29	30	31	32	34
25.0-29.9	7	12	20	25	27	29	31	32	33	35	30
30.0-34.9	8	14	22	26	29	31	33	35	36	37	39
35.0-39.9	9	16	23	28	30	32	35	36	37	39	41 42
40.0-49.9	10	17	24	29	32	34	36	38	39	41	42 46
50.0-59.9	12	21	26	31	34	36	39	41	42	44	40
60.0-69.9	14	22 23	27	33	36	39	42	43	45	47 49	49 51
70.0-79.9	16	23	29	35	38	41 42	44 46	46 48	47 49	51	54
80.0-89.9	17	25	30	36	40	44	46 48	50	51	53	56
90.0-99.9	19	26	31	38	42	46	46	50 52	53	55	56 58
100.0-119.9	21	26	32	39 42	43	46 49	52	55	56	59	61
120.0-139.9	22	28	35 36	42	46 48	51	52 55	58	59	62	65
140.0-159.9	23	30	36 38	44 46	50	54	58	60	62	65	67
160.0-179.9	25	31		48	50 52	56	60	63	65	67	70
180.0-199.9	26	32	40	48 49	52 54	58	62	65	67	69	70 73
>199.9	26	33	41	47	24	20	02	60	0/	07	,

Appendix VII. - Health-Based Limits for Exclusion of Waste-Derived Residues\*

	Metals - TCLP Extract Concentration Limits			
Constituent	CAS No.	Concentration Limits (mg/kg)		
Antimony	7440-36-0	1xE+00		
Arsenic	7440-38-2	5xE+00		
Barium	7440-39-3	1xE+02		
Beryllium	7440-41-7	7xE-03		
Cadmium	7440-43-9	1xE+00		
Chromium	7440-47-3	5xE+00		
Lead	7439-92-1	5xE+00		
Mercury	7439-97-6	2xE-01		
Nickel	7440-02-0	7xE+01		
Selenium	7782-49-2	1xE+00		
Silver	7440-22-4	5xE+00		

Nonmetals - Residue Concentration Limits			
		Concentration	
		Limits for	
<u>Constituent</u>	CAS No.	Residues(mg/kg)	
Acetonitrile	75-05-8	2xE-01	
Acetophenone	98-86-2	4xE+00	
Acrolein	107-02-8	5xE-01	
Acrylamide	79-06-1	2xE-04	
Acrylonitrile	107-13-1	7xE-04	
Aldrin	309-00-2	2xE-05	
Allyl alcohol	107-18-6	2xE-01	
Aluminum phosphide	20859-73-8	1xE-02	
Aniline	62-53-3	6xE-02	
Barium cyanide	542-62-1	1xE+00	
Benz(a)anthracene	56-55-3	1xE-04	
Benzene	71-43-2	5xE-03	
Benzidine	92-87-5	1xE-06	
Bis(2-chloroethyl) ether	111-44-4	3xE-04	
Bis(chloromethyl) ether	542-88-1	2xE-06	
Bis(2-ethylhexyl) phthalate	117-81-7	3xE+01	
Bromoform	75-25-2	7xE-01	
Calcium cyanide	592-01-8	1xE-06	
Carbon disulfide	75-15-0	4xE+00	
Carbon tetrachloride	56-23-5	5xE-03	
Chlordane	57-74-9	3xE-04	
Chlorobenzene	108-90-7	1xE+00	
Chloroform	67-66-3	6xE-02	
Copper cyanide	544-92-3	2xE-01	
Cresols (Cresylic acid)	1319-77-3	2xE+00	

Nonmetals - Residue Concentration Limits				
		Concentration		
		Limits for		
Constituent	CAS No.	Residues(mg/kg)		
Cyanogen	460-19-5	1xE+00		
DDT	-50-29-3	1xE-03		
Dibenz(a,h)anthracene	53-70-3	7xE-06		
1.2-Dibromo-3-chloropropane	96-12-8	2xE-05		
p-Dichlorobenzene	106-46-7	7.5xE-02		
Dichlorodifluoromethane	75-71-8	7xE+00		
1,1-Dichloroethylene	75-35-4	5xE-03		
2,4-Dichlorophenol	120-83-2	1xE-01		
1.3-Dichloropropene	542-75-6	1xE-03		
Dieldrin	60-57-1	2xE-05		
Diethyl phthalate	84-66-2	3xE+01		
Diethylstilbesterol	56-53-1	7xE-07		
Dimethoate	60-51-5	3xE-02		
2,4-Dinitrotoluene	121-14-2	5xE-04		
Diphenylamine	122-39-4	9xE-01		
1,2-Diphenylhydrazine	122-66-7	5xE-04		
Endosulfan	115-29-7	2xE-03		
Endrin	72-20-8	2xE-04		
Epichlorohydrin	106-89-8	4xE-02		
Ethylene dibromide	106-93-4	4xE-07		
Ethylene oxide	75-21-8	3xE-04		
Fluorine	7782-41-4	4xE+00		
Formic acid	64-18-6	7F+01		
Heptachlor	76-44-8	8xE-05		
Heptachlor epoxide	1024-57-3	4xE-05		
Hexachlorobenzene	118-74-1	2xE-04		
Hexachlorobutadiene	87-68-3	5xE-03		
Hexachlorocyclopentadiene	77-47-4	2xE-01		
Hexachlorodibenzo-p-dioxins	19408-74-3	6xE-08		
Hexachloroethane	67-72-1	3xE-02		
	302-01-1	1xE-04		
Hydrazine	74-90-8	7xE-05		
Hydrogen cyanide	7783-06-4	1xE-06		
Hydrogen sulfide	78-83-1	1xE+01		
Isobutyl alcohol	16752-77-5	1xE+00		
Methomyl		1xE-01		
Methoxychlor	72-43-5			
3-Methylcholanthrene	56-49-5	4xE-05		
4,4'-Methylenebis(2-chlorosniline)	101-14-4	2xE-03		
Methylene chloride	75-09-2	5xE-02		
Methyl ethyl ketone (MEK)	78-93-3	2xE+00		
Methyl hydrazine	60-34-4	3xE-04		
Methyl parathion	298-00-0	2xE-02		
Naphthalene	91-20-3	1xE+01		
Nickel cyanide	557-19-7	7xE-01		
Nitric oxide				
MICTIC OXIGE	10102-43-9 98-95-3	4xE+00 2xE-02		

1,1,2-Trichloroethane

Trichloroethylene

Nonmetals - Residue Concentration Limits Concentration Limits for CAS No. Residues(mg/kg) Constituent 6xE-05 924-16-3 N-Nitrosodi-n-butylamine 55-18-5 2xE-06 N-Nitrosodiethylamine 684-93-5 1xE-07 N-Nitroso-N-methylurea 930-55-2 2xE-04 N-Nitrosopyrrolidine 608-93-5 3xE-02 Pentachlorobenzene 82-68-8 1xE-01 Pentachloronitrobenzene (PCNB) 87-86-5 1xE+00 Pentachlorophenol 108-95-2 1xE+00 Phenol 3xE-03 62-38-4 Phenylmercury acetate 1xE-02 7803-51-2 Phosphine 1336-36-3 5xE-05 Polychlorinated biphenyls, N.O.S. 151-50-8 2xE+00 Potassir cyanide 506-61-6 7xE+00Potass: silver cyanide 23950-58-5 3xE+00Pronami 4xE-02 110-86-1 Pyridin 3xE-05 50-55-5 Reserpi: 2xE-01 630-10-4 Selenou. a 506-64-9 4xE+00 Silver cyanide 1xE+00 143-33-9 Sodium cyanide 57-24-9 1xE-02 Strychnine 95-94-3 1xE-02 1,2,4,5-Tetrachlorobenzene 2xE-03 79-34-5 1,1,2,2-tetrachloroethane 127-18-4 7xE-01 Tetrachloroethylene 58-90-2 1xE-02 2,3,4,6-Tetrachlorophenol 4xE-06 78-00-2 Tetraethyl lead 7440-28-0 7xE+00 Thallium 2xE-03 1314-32-5 Thallic oxide 3xE-03 563-68-8 Thallium(I) acetate 3xE-03 Thallium(I) carbonate 6533-73-9 Thai :um(I) chloride 7791-12-0 3xE-03 10102-45-1 3xE-03 Thal .um(I) nitrate 3xE-03 12039-52-0 Thallium selenite 3xE-03 Thallium(I) sulfate 7446-18-6 62-56-6 2xE-04 Thiourea 108-88-3 1xE+01 Toluene 8001-35-2 5xE-03 Toxaphene

79-00-5

79-01-6

6xE-03

5xE-03

Nonmetals - Residue Concentration Limits		
		Concentration Limits for
Constituent	CAS No.	Residues(mg/kg)
Trichloromonofluoromethane	75-69-4	1xE+01
2,4,5-Trichlorophenol	95-95-4	4xE+00
2,4,6-Trichlorophenol	88-06-2	4xE+00
Vanadium pentoxide	1314-62-1	7xE-01
Vinyl chloride	75-01-4	2xE-03

<sup>\*</sup> The health-based concentration limits for Appendix VIII Part 261 constituents for which a health-based concentration is not provided below is 2xE-06 mg/kg.

### Appendix VIII. - Potential PICs for Determination of Exclusion of Waste-Derived Residues

## PICs FOUND IN STACK EFFLUENTS

------Volatiles Semivolatiles 

Toluene Carbon tetrachloride Chloroform

Methylene chloride Trichloroethylene Tetrachloroethylene 1,1,1-Trichloroethane m-Dichlorobenzene

Benzene

Bromochloromethane Bromodichloromethane

Bromoform Bromomethane Methylene bromide Methyl ethyl ketone Bis(2-ethylhexyl)phthalate

Naphthalene

Phenol

Diethyl phthalate Butyl benzyl phthalate 2,4-Dimethylphenol o-Dichlorobenzene Chlorobenzene p-Dichlorobenzene cis-1,4-Dichloro-2-butene Hexachlorobenzene 2,4,6-Trichlorophenol

> Fluoranthene o-Nitrophenol

1,2,4-Trichlorobenzene

o-Chlorophenol Pentachlorophenol

Pyrene

Dimethyl phthalate Mononitrobenzene

2,6-Toluene diisocyanate